

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
26 July 2001 (26.07.2001)

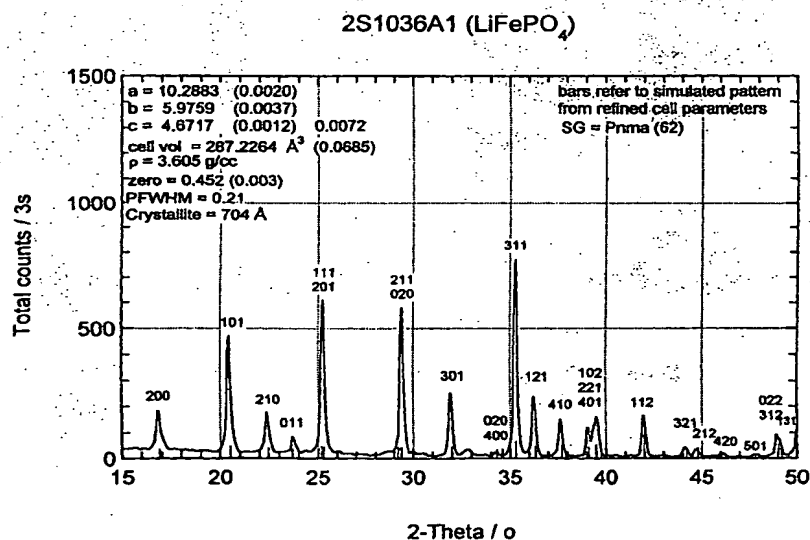
PCT

(10) International Publication Number  
WO 01/53198 A1

- (51) International Patent Classification<sup>7</sup>: C01B 25/37, 25/45, H01M 4/58
- (21) International Application Number: PCT/US00/35438
- (22) International Filing Date:  
22 December 2000 (22.12.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
09/484,919 18 January 2000 (18.01.2000) US
- (63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:  
US 09/484,919 (CON)  
Filed on 18 January 2000 (18.01.2000)
- (71) Applicant (for all designated States except US): VALLENCE TECHNOLOGY, INC. [US/US]; 301 Conestoga Way, Henderson, NV 89015 (US).
- (72) Inventors; and  
(75) Inventors/Applicants (for US only): BARKER, Jeremy [GB/GB]; 5 Little Acreage, Oxford OX3 0PS (GB). SAIDI, M., Yazid [DZ/US]; 301 Conestoga Way, Henderson, NV 89015 (US). SWOYER, Jeffrey, L. [US/US]; 301 Conestoga Way, Henderson, NV 89015 (US).
- (74) Agent: DESCHERE, Linda, M.; Harness, Dickey & Pierce, P.L.C., Suite 400, 5445 Corporate Drive, Troy, MI 48098 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW); Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM); European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,

[Continued on next page]

(54) Title: PREPARATION OF LITHIUM-CONTAINING MATERIALS



(57) Abstract: The invention provides novel lithium-mixed metal materials which, upon electrochemical interaction, release lithium ions, and are capable of reversibly cycling lithium ions. The invention provides a rechargeable lithium battery which comprises an electrode formed from the novel lithium-mixed metal materials. Methods for making the novel lithium-mixed metal materials and methods for using such lithium-mixed metal materials in electrochemical cells are also provided. The lithium-mixed metal materials comprise lithium and at least one other metal besides lithium. Preferred materials are lithium-mixed metal phosphates which contain lithium and two other metals besides lithium.

## WO 01/53198 A1



IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

## PREPARATION OF LITHIUM-CONTAINING MATERIALS

### Field of the Invention

This invention relates to improved materials  
5 usable as electrode active materials and to their  
preparation.

### Background of the Invention

Lithium batteries are prepared from one or more  
lithium electrochemical cells containing  
10 electrochemically active (electroactive) materials. Such  
cells typically include an anode (negative electrode), a  
cathode (positive electrode), and an electrolyte  
interposed between spaced apart positive and negative  
electrodes. Batteries with anodes of metallic lithium  
15 and containing metal chalcogenide cathode active material  
are known. The electrolyte typically comprises a salt of  
lithium dissolved in one or more solvents, typically  
nonaqueous (aprotic) organic solvents. Other  
electrolytes are solid electrolytes typically called  
20 polymeric matrixes that contain an ionic conductive  
medium, typically a metallic powder or salt, in  
combination with a polymer that itself may be ionically  
conductive which is electrically insulating. By  
convention, during discharge of the cell, the negative  
25 electrode of the cell is defined as the anode. Cells  
having a metallic lithium anode and metal chalcogenide  
cathode are charged in an initial condition. During  
discharge, lithium ions from the metallic anode pass  
through the liquid electrolyte to the electrochemical

active (electroactive) material of the cathode whereupon they release electrical energy to an external circuit.

It has recently been suggested to replace the lithium metal anode with an insertion anode, such as a lithium metal chalcogenide or lithium metal oxide. Carbon anodes, such as coke and graphite, are also insertion materials. Such negative electrodes are used with lithium- containing insertion cathodes, in order to form an electroactive couple in a cell. Such cells, in an initial condition, are not charged. In order to be used to deliver electrochemical energy, such cells must be charged in order to transfer lithium to the anode from the lithium- containing cathode. During discharge, the lithium is transferred from the anode back to the cathode. During a subsequent recharge, the lithium is transferred back to the anode where it re-inserts. Upon subsequent charge and discharge, the lithium ions ( $\text{Li}^+$ ) are transported between the electrodes. Such rechargeable batteries, having no free metallic species are called rechargeable ion batteries or rocking chair batteries. See U.S. Patent Nos. 5,418,090; 4,464,447; 4,194,062; and 5,130,211.

Preferred positive electrode active materials include  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiNiO}_2$ . The cobalt compounds are relatively expensive and the nickel compounds are difficult to synthesize. A relatively economical positive electrode is  $\text{LiMn}_2\text{O}_4$ , for which methods of synthesis are known. The lithium cobalt oxide ( $\text{LiCoO}_2$ ), the lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ), and the lithium nickel oxide ( $\text{LiNiO}_2$ ) all have a common disadvantage in that the charge capacity of a cell comprising such cathodes suffers a significant loss in capacity. That

is, the initial capacity available (amp hours/gram) from  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , and  $\text{LiCoO}_2$  is less than the theoretical capacity because significantly less than 1 atomic unit of lithium engages in the electrochemical reaction. Such an  
5 initial capacity value is significantly diminished during the first cycle operation and such capacity further diminishes on every successive cycle of operation. For  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$  only about 0.5 atomic units of lithium is reversibly cycled during cell operation. Many  
10 attempts have been made to reduce capacity fading, for example, as described in U.S. Patent No. 4,828,834 by Nagaura et al. However, the presently known and commonly used, alkali transition metal oxide compounds suffer from relatively low capacity. Therefore, there remains the  
15 difficulty of obtaining a lithium-containing electrode material having acceptable capacity without disadvantage of significant capacity loss when used in a cell.

Summary of the Invention

The invention provides novel lithium-mixed metal materials which, upon electrochemical interaction, release lithium ions, and are capable of reversibly cycling lithium ions. The invention provides a rechargeable lithium battery which comprises an electrode formed from the novel lithium-mixed metal materials. Methods for making the novel lithium-mixed metal materials and methods for using such lithium-mixed metal materials in electrochemical cells are also provided. The lithium-mixed metal materials comprise lithium and at least one other metal besides lithium. Preferred materials are lithium-mixed metal phosphates which contain lithium and two other metals besides lithium. Accordingly, the invention provides a rechargeable lithium battery which comprises an electrolyte; a first electrode having a compatible active material; and a second electrode comprising the novel materials. In one aspect, the novel materials are lithium-mixed metal phosphates which preferably used as a positive electrode active material, reversibly cycle lithium ions with the compatible negative electrode active material. Desirably, the lithium-mixed metal phosphate is represented by the nominal general formula  $\text{Li}_a\text{MI}_b\text{MII}_c(\text{PO}_4)_d$ . Such compounds include  $\text{Li}_1\text{MI}_a\text{MII}_b\text{PO}_4$  and  $\text{Li}_3\text{MI}_a\text{MII}_b(\text{PO}_4)_3$ ; therefore, in an initial condition  $0 \leq a \leq 1$  or  $0 \leq a \leq 3$ , respectively. During cycling, x quantity of lithium is released where  $0 \leq x \leq a$ . In the general formula, the sum of b plus c is up to about 2. Specific examples are  $\text{Li}_1\text{MI}_{1-y}\text{MII}_y\text{PO}_4$  and  $\text{Li}_3\text{MI}_{2-y}\text{MII}_y(\text{PO}_4)_3$ .

In one aspect, MI and MII are the same. In a preferred aspect, MI and MII are different from one

5.

another. At least one of MI and MII is an element capable of an oxidation state higher than that initially present in the lithium-mixed metal phosphate compound. Correspondingly, at least one of MI and MII has more than one oxidation state in the phosphate compound, and more than one oxidation state above the ground state  $M^0$ . The term oxidation state and valence state are used in the art interchangeably.

In another aspect, both MI and MII may have more than one oxidation state and both may be oxidizable from the state initially present in the phosphate compound. Desirably, MII is a metal or semi-metal having a +2 oxidation state, and is selected from Groups 2, 12 and 14 of the Periodic Table. Desirably, MII is selected from non-transition metals and semi-metals. In one embodiment, MII has only one oxidation state and is nonoxidizable from its oxidation state in the lithium-mixed metal compound. In another embodiment, MII has more than one oxidation state. Examples of semi-metals having more than one oxidation state are selenium and tellurium; other non-transition metals with more than one oxidation state are tin and lead. Preferably, MII is selected from Mg (magnesium), Ca (calcium), Zn (zinc), Sr (strontium), Pb (lead), Cd (cadmium), Sn (tin), Ba (barium), and Be (beryllium), and mixtures thereof. In another preferred aspect, MII is a metal having a +2 oxidation state and having more than one oxidation state, and is oxidizable from its oxidation state in lithium-mixed metal compound.

Desirably, MI is selected from Fe (iron), Co (cobalt), Ni (nickel), Mn (manganese), Cu (copper), V (vanadium), Sn (tin), Ti (titanium), Cr (chromium), and



WO 01/53198

PCT/US00/35438

6

mixtures thereof. As can be seen, MI is preferably selected from the first row of transition metals and further includes tin, and MI preferably initially has a +2 oxidation state.

5 In a preferred aspect, the product  $\text{LiMI}_{1-y}\text{MII}_y\text{PO}_4$  is an olivine structure and the product  $\text{Li}_3\text{MI}_{1-y}(\text{PO}_4)_3$  is a rhombohedral or monoclinic Nasicon structure. In another aspect, the term "nominal formula" refers to the fact that the relative proportion of atomic species may vary  
10 slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent. In still another aspect, any portion of P (phosphorous) may be substituted by Si (silicon), S (sulfur), and/or As (arsenic); and any portion of O (oxygen) may be substituted by halogen,  
15 preferably F (fluorine). These aspects are also disclosed in U.S. Patent Application Serial Numbers 09/105,748 filed June 26, 1998, and 09/274,371 filed March 23, 1999; and in U.S. Patent No. 5,871,866 issued February 16, 1999, which is incorporated by reference in  
20 its entirety; each of the listed applications and patents are co-owned by the assignee of the present invention.

The metal phosphates are alternatively represented by the nominal general formulas such as  $\text{Li}_{1-x}\text{MI}_{1-y}\text{MII}_y\text{PO}_4$  ( $0 \leq x \leq 1$ ), and  $\text{Li}_{3-x}\text{MI}_{2-y}\text{MII}_y(\text{PO}_4)_3$   
25 signifying capability to release and reinsert lithium. The term "general" refers to a family of compounds, with M, x and y representing variations therein. The expressions 2-y and 1-y each signify that the relative amount of MI and MII may vary. In addition, as stated  
30 above, MI may be a mixture of metals meeting the earlier stated criteria for MI. In addition, MII may be a mixture of metallic elements meeting the stated criteria

for MII. Preferably, where MII is a mixture, it is a mixture of 2 metallic elements; and where MI is a mixture, it is a mixture of 2 metals. Preferably, each such metal and metallic element has a +2 oxidation state in the initial phosphate compound.

The active material of the counter electrode is any material compatible with the lithium-mixed metal phosphate of the invention. Where the lithium-mixed metal phosphate is used as a positive electrode active material, metallic lithium, lithium-containing material, or non-lithium-containing material may be used as the negative electrode active material. The negative electrode is desirably a nonmetallic insertion material. Desirably, the negative electrode comprises an active material from the group consisting of metal oxide, particularly transition metal oxide, metal chalcogenide, carbon, graphite, and mixtures thereof. It is preferred that the anode active material comprises a carbonaceous material such as graphite. The lithium-mixed metal phosphate of the invention may also be used as a negative electrode material.

In another embodiment, the present invention provides a method of preparing a compound of the nominal general formula  $\text{Li}_a\text{MI}_b\text{MII}_c(\text{PO}_4)_d$  where  $0 < a \leq 3$ ; the sum of  $b$  plus  $c$  is greater than zero and up to about 2; and  $0 < d \leq 3$ . Preferred compounds include  $\text{Li}_3\text{MI}_b\text{MII}_c(\text{PO}_4)_3$  where  $b$  plus  $c$  is about 2; and  $\text{LiMI}_b\text{MII}_c\text{PO}_4$  where  $b$  plus  $c$  is about 1. The method comprises providing starting materials in particle form. The starting (precursor) materials include a lithium-containing compound, one or more metal containing compounds, a compound capable of providing the phosphate  $(\text{PO}_4)^{-3}$  anion, and carbon.

WO 01/53198

PCT/US00/35438

8

Preferably, the lithium-containing compound is in particle form, and an example is lithium salt.

Preferably, the phosphate-containing anion compound is in particle form, and examples include metal phosphate salt and diammonium hydrogen phosphate (DAHP) and ammonium dihydrogen phosphate (ADHP). The lithium compound, one or more metal compounds, and phosphate compound are included in a proportion which provides the stated nominal general formula. The starting materials are mixed together with carbon, which is included in an amount sufficient to reduce the metal ion of one or more of the metal-containing starting materials without full reduction to an elemental metal state. Excess quantities of carbon and one or more other starting materials (i.e., 5 to 10% excess) may be used to enhance product quality. A small amount of carbon, remaining after the reaction, functions as a conductive constituent in the ultimate electrode formulation. This is an advantage since such remaining carbon is very intimately mixed with the product active material. Accordingly, large quantities of excess carbon, on the order of 100% excess carbon are useable in the process. The carbon present during compound formation is thought to be intimately dispersed throughout the precursor and product. This provides many advantages, including the enhanced conductivity of the product. The presence of carbon particles in the starting materials is also thought to provide nucleation sites for the production of the product crystals.

The starting materials are intimately mixed and then reacted together where the reaction is initiated by heat and is preferably conducted in a nonoxidizing, inert atmosphere, whereby the lithium, metal from the metal compound(s), and phosphate combine to form the

$\text{Li}_a\text{MI}_b\text{MII}_c(\text{PO}_4)_d$  product. Before reacting the compounds, the particles are intermingled to form an essentially homogeneous powder mixture of the precursors. In one aspect, the precursor powders are dry-mixed using a ball mill, such as zirconia media. Then the mixed powders are pressed into pellets. In another aspect, the precursor powders are mixed with a binder. The binder is selected so as to not inhibit reaction between particles of the powders. Therefore, preferred binders decompose or evaporate at a temperature less than the reaction temperature. Examples include mineral oils (i.e., glycerol, or C-18 hydrocarbon mineral oil) and polymers which decompose (carbonize) to form a carbon residue before the reaction starts, or which evaporate before the reaction starts. In still another aspect, intermingling is conducted by forming a wet mixture using a volatile solvent and then the intermingled particles are pressed together in pellet form to provide good grain-to-grain contact.

Although it is desired that the precursor compounds be present in a proportion which provides the stated general formula of the product, the lithium compound may be present in an excess amount on the order of 5 percent excess lithium compared to a stoichiometric mixture of the precursors. And the carbon may be present at up to 100% excess compared to the stoichiometric amount. The method of the invention may also be used to prepare other novel products, and to prepare known products. A number of lithium compounds are available as precursors, such as lithium acetate ( $\text{LiOOCCH}_3$ ), lithium hydroxide, lithium nitrate ( $\text{LiNO}_3$ ), lithium oxalate ( $\text{Li}_2\text{C}_2\text{O}_4$ ), lithium oxide ( $\text{Li}_2\text{O}$ ), lithium phosphate ( $\text{Li}_3\text{PO}_4$ ), lithium dihydrogen phosphate ( $\text{LiH}_2\text{PO}_4$ ), lithium

vanadate ( $\text{LiVO}_3$ ), and lithium carbonate ( $\text{Li}_2\text{CO}_3$ ). The lithium carbonate is preferred for the solid state reaction since it has a very high melting point and commonly reacts with the other precursors before melting.

5 Lithium carbonate has a melting point over  $600^\circ\text{C}$  and it decomposes in the presence of the other precursors and/or effectively reacts with the other precursors before melting. In contrast, lithium hydroxide melts at about  $400^\circ\text{C}$ . At some reaction temperatures preferred herein of

10 over  $450^\circ\text{C}$  the lithium hydroxide will melt before any significant reaction with the other precursors occurs to an effective extent. This melting renders the reaction very difficult to control. In addition, anhydrous  $\text{LiOH}$  is highly hygroscopic and a significant quantity of water

15 is released during the reaction. Such water needs to be removed from the oven and the resultant product may need to be dried. In one preferred aspect, the solid state reaction made possible by the present invention is much preferred since it is conducted at temperatures at which

20 the lithium-containing compound reacts with the other reactants before melting. Therefore, lithium hydroxide is useable as a precursor in the method of the invention in combination with some precursors, particularly the phosphates. The method of the invention is able to be

25 conducted as an economical carbothermal-based process with a wide variety of precursors and over a relatively broad temperature range.

The aforesaid precursor compounds (starting materials) are generally crystals, granules, and powders

30 and are generally referred to as being in particle form. Although many types of phosphate salts are known, it is preferred to use diammonium hydrogen phosphate  $(\text{NH}_4)_2\text{HPO}_4$  (DAHP) or ammonium dihydrogen phosphate  $(\text{NH}_4)\text{H}_2\text{PO}_4$  (ADHP).

Both ADHP and DAHP meet the preferred criteria that the precursors decompose in the presence of one another or react with one another before melting of such precursor. Exemplary metal compounds are  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{VO}_2$ ,  $\text{LiVO}_3$ ,  $\text{NH}_4\text{VO}_3$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3(\text{PO}_4)_2$ ,  $\text{CuO}$ ,  $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{PbO}_2$ ,  $\text{PbO}$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{BaO}$ ,  $\text{Cd}(\text{OH})_2$ . In addition, some starting materials serve as both the source of metal ion and phosphate, such as  $\text{FePO}_4$ ,  $\text{Fe}_3(\text{PO}_4)_2$ ,  $\text{Zn}_3(\text{PO}_4)_2$ , and  $\text{Mg}_3(\text{PO}_4)_2$ . Still others contain both lithium ion and phosphate such as  $\text{Li}_3\text{PO}_4$  and  $\text{LiH}_2\text{PO}_4$ . Other exemplary precursors are  $\text{H}_3\text{PO}_4$  (phosphoric acid); and  $\text{P}_2\text{O}_5$  ( $\text{P}_4\text{O}_{10}$ ) phosphoric oxide; and  $\text{HPO}_3$  meta phosphoric acid, which is a decomposition product of  $\text{P}_2\text{O}_5$ . If it is desired to replace any of the oxygen with a halogen, such as fluorine, the starting materials further include a fluorine compound such as  $\text{LiF}$ . If it is desired to replace any of the phosphorous with silicon, then the starting materials further include silicon oxide ( $\text{SiO}_2$ ). Similarly, ammonium sulfate in the starting materials is useable to replace phosphorus with sulfur.

The starting materials are available from a number of sources. The following are typical. Vanadium pentoxide of the formula  $\text{V}_2\text{O}_5$  is obtainable from any number of suppliers including Kerr McGee, Johnson Matthey, or Alpha Products of Davers, Massachusetts. Vanadium pentoxide has a CAS number of 1314-62-1. Iron oxide  $\text{Fe}_3\text{O}_3$  is a common and very inexpensive material available in powder form from the same suppliers. The other precursor materials mentioned above are also available from well known suppliers, such as those listed above.

The method of the invention may also be used to react starting materials in the presence of carbon to form a variety of other novel products, such as gamma-LiV<sub>2</sub>O<sub>5</sub> and also to produce known products. Here, the carbon functions to reduce metal ion of a starting metal compound to provide a product containing such reduced metal ion. The method is particularly useful to also add lithium to the resultant product, which thus contains the metallic element ions, namely, the lithium ion and the other metal ion, thereby forming a mixed metal product. An example is the reaction of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) with lithium carbonate in the presence of carbon to form gamma-LiV<sub>2</sub>O<sub>5</sub>. Here the starting metal ion V<sup>+5</sup>V<sup>+5</sup> is reduced to V<sup>+4</sup>V<sup>+5</sup> in the final product. A single phase gamma-LiV<sub>2</sub>O<sub>5</sub> product is not known to have been directly and independently formed before.

As described earlier, it is desirable to conduct the reaction at a temperature where the lithium compound reacts before melting. The temperature should be about 400°C or greater, and desirably 450°C or greater, and preferably 500°C or greater, and generally will proceed at a faster rate at higher temperatures. The various reactions involve production of CO or CO<sub>2</sub> as an effluent gas. The equilibrium at higher temperature favors CO formation. Some of the reactions are more desirably conducted at temperatures greater than 600°C; most desirably greater than 650°C; preferably 700°C or greater; more preferably 750°C or greater. Suitable ranges for many reactions are about 700 to 950°C, or about 700 to 800°C.

Generally, the higher temperature reactions produce CO effluent and the stoichiometry requires more

carbon be used than the case where CO<sub>2</sub> effluent is produced at lower temperature. This is because the reducing effect of the C to CO<sub>2</sub> reaction is greater than the C to CO reaction. The C to CO<sub>2</sub> reaction involves an increase in carbon oxidation state of +4 (from 0 to 4) and the C to CO reaction involves an increase in carbon oxidation state of +2 (from ground state zero to 2). Here, higher temperature generally refers to a range of about 650°C to about 1000°C and lower temperature refers to up to about 650°C. Temperatures higher than 1200°C are not thought to be needed.

In one aspect, the method of the invention utilizes the reducing capabilities of carbon in a unique and controlled manner to produce desired products having structure and lithium content suitable for electrode active materials. The method of the invention makes it possible to produce products containing lithium, metal and oxygen in an economical and convenient process. The ability to lithiate precursors, and change the oxidation state of a metal without causing abstraction of oxygen from a precursor is heretofore unexpected. These advantages are at least in part achieved by the reductant, carbon, having an oxide whose free energy of formation becomes more negative as temperature increases. Such oxide of carbon is more stable at high temperature than at low temperature. This feature is used to produce products having one or more metal ions in a reduced oxidation state relative to the precursor metal ion oxidation state. The method utilizes an effective combination of quantity of carbon, time and temperature to produce new products and to produce known products in a new way.



Referring back to the discussion of temperature, at about 700°C both the carbon to carbon monoxide and the carbon to carbon dioxide reactions are occurring. At closer to 600°C the C to CO<sub>2</sub> reaction is the dominant reaction. At closer to 800°C the C to CO reaction is dominant. Since the reducing effect of the C to CO<sub>2</sub> reaction is greater, the result is that less carbon is needed per atomic unit of metal to be reduced. In the case of carbon to carbon monoxide, each atomic unit of carbon is oxidized from ground state zero to plus 2. Thus, for each atomic unit of metal ion (M) which is being reduced by one oxidation state, one half atomic unit of carbon is required. In the case of the carbon to carbon dioxide reaction, one quarter atomic unit of carbon is stoichiometrically required for each atomic unit of metal ion (M) which is reduced by one oxidation state, because carbon goes from ground state zero to a plus 4 oxidation state. These same relationships apply for each such metal ion being reduced and for each unit reduction in oxidation state desired.

It is preferred to heat the starting materials at a ramp rate of a fraction of a degree to 10°C per minute and preferably about 2°C per minute. Once the desired reaction temperature is attained, the reactants (starting materials) are held at the reaction temperature for several hours. The heating is preferably conducted under non-oxidizing or inert gas such as argon or vacuum. Advantageously, a reducing atmosphere is not required, although it may be used if desired. After reaction, the products are preferably cooled from the elevated temperature to ambient (room) temperature (i.e., 10°C to 40°C). Desirably, the cooling occurs at a rate similar to the earlier ramp rate, and preferably 2°C/minute

cooling. Such cooling rate has been found to be adequate to achieve the desired structure of the final product. It is also possible to quench the products at a cooling rate on the order of about 100°C/minute. In some instances, such rapid cooling (quench) may be preferred.

The present invention resolves the capacity problem posed by widely used cathode active material. It has been found that the capacity and capacity retention of cells having the preferred active material of the invention are improved over conventional materials. Optimized cells containing lithium-mixed metal phosphates of the invention potentially have performance improved over commonly used lithium metal oxide compounds. Advantageously, the new method of making the novel lithium-mixed metal phosphate compounds of the invention is relatively economical and readily adaptable to commercial production.

Objects, features, and advantages of the invention include an electrochemical cell or battery based on lithium-mixed metal phosphates. Another object is to provide an electrode active material which combines the advantages of good discharge capacity and capacity retention. It is also an object of the present invention to provide electrodes which can be manufactured economically. Another object is to provide a method for forming electrode active material which lends itself to commercial scale production for preparation of large quantities.

WO 01/53198

PCT/US00/35438

16

These and other objects, features, and advantages will become apparent from the following description of the preferred embodiments, claims, and accompanying drawings.

### Brief Description of the Drawings

**Figure 1** shows the results of an x-ray diffraction analysis, of the  $\text{LiFePO}_4$  prepared according to the invention using  $\text{CuK}\alpha$  radiation,  $\lambda = 1.5405\text{\AA}$ . Bars refer to simulated pattern from refined cell parameters, Space Group, SG = Pnma (62). The values are  $a = 10.2883\text{\AA}$  (0.0020),  $b = 5.9759\text{\AA}$  (0.0037),  $c = 4.6717\text{\AA}$  (0.0012) 0.0072, cell volume =  $287.2264\text{\AA}^3$  (0.0685). Density,  $\rho = 3.605 \text{ g/cc}$ , zero = 0.452 (0.003). Peak at full width half maximum, PFWHM = 0.21. Crystallite size from XRD data =  $704\text{\AA}$ .

**Figure 2** is a voltage/capacity plot of  $\text{LiFePO}_4$ -containing cathode cycled with a lithium metal anode using constant current cycling at  $\pm 0.2$  milliamps per square centimeter in a range of 2.5 to 4.0 volts at a temperature of about  $23^\circ\text{C}$ . The cathode contained 19.0mg of the  $\text{LiFePO}_4$  active material, prepared by the method of the invention. The electrolyte comprised ethylene carbonate (EC) and dimethyl carbonate (DMC) in a weight ratio of 2:1 and included a 1 molar concentration of  $\text{LiPF}_6$  salt. The lithium-metal-phosphate containing electrode and the lithium metal counter electrode are maintained spaced apart by a glass fiber separator which is interpenetrated by the solvent and the salt.

**Figure 3** shows multiple constant current cycling of  $\text{LiFePO}_4$  active material cycled with a lithium metal anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at  $\pm 0.2$  milliamps per square centimeter, 2.5 to 4.0 volts at two different temperature conditions,  $23^\circ\text{C}$  and  $60^\circ\text{C}$ . **Figure 3** shows the excellent rechargeability of

the lithium iron phosphate/lithium metal cell, and also shows the excellent cycling and specific capacity (mAh/g) of the active material.

**Figure 4** shows the results of an x-ray diffraction analysis, of the  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  prepared according to the invention, using  $\text{CuK}\alpha$  radiation,  $\lambda = 1.5405\text{\AA}$ . Bars refer to simulated pattern from refined cell parameters SG = Pnma (62). The values are  $a = 10.2688\text{\AA}$  (0.0069),  $b = 5.9709\text{\AA}$  (0.0072),  $c = 4.6762\text{\AA}$  (0.0054), cell volume =  $286.7208\text{\AA}^3$  (0.04294),  $p = 3.617$  g/cc, zero = 0.702 (0.003), PFWHM = 0.01, and crystallite =  $950\text{\AA}$ .

**Figure 5** is a voltage/capacity plot of  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ -containing cathode cycled with a lithium metal anode using constant current cycling at  $\pm 0.2$  milliamps per square centimeter in a range of 2.5 to 4.0 volts. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 18.9mg of the  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  active material prepared by the method of the invention.

**Figure 6** shows multiple constant current cycling of  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  cycled with a lithium metal anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at  $\pm 0.2$  milliamps per square centimeter, 2.5 to 4.0 volts at two different temperature conditions,  $23^\circ\text{C}$  and  $60^\circ\text{C}$ . **Figure 6** shows the excellent rechargeability of the lithium-metal-phosphate/lithium metal cell, and also shows the excellent cycling and capacity of the cell.

**Figure 7** is a voltage/capacity plot of  $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ -containing cathode cycled with a lithium metal anode using constant current cycling at  $\pm 0.2$  milliamps per square centimeter in a range of 2.5 to 4.0 volts at 23°C. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 16mg of the  $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$  active material prepared by the method of the invention.

**Figure 8** shows the results of an x-ray diffraction analysis, of the  $\text{LiFe}_{0.9}\text{Ca}_{0.1}\text{PO}_4$  prepared according to the invention, using  $\text{CuK}\alpha$  radiation,  $\lambda = 1.5405\text{\AA}$ . Bars refer to simulated pattern from refined cell parameters SG = Pnma (62). The values are  $a = 10.3240\text{\AA}$  (0.0045),  $b = 6.0042\text{\AA}$  (0.0031),  $c = 4.6887\text{\AA}$  (0.0020), cell volume =  $290.6370\text{\AA}^3$  (0.1807), zero = 0.702 (0.003),  $\rho = 3.62$  g/cc, PFWHM = 0.18, and crystallite =  $680\text{\AA}$ .

**Figure 9** is a voltage/capacity plot of  $\text{LiFe}_{0.8}\text{Ca}_{0.2}\text{PO}_4$ -containing cathode cycled with a lithium metal anode using constant current cycling at  $\pm 0.2$  milliamps per square centimeter in a range of 2.5 to 4.0 volts at 23°. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 18.5mg of the  $\text{LiFe}_{0.8}\text{Ca}_{0.2}\text{PO}_4$  active material prepared by the method of the invention.

**Figure 10** is a voltage/capacity plot of  $\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$ -containing cathode cycled with a lithium metal anode using constant current cycling at  $\pm 0.2$  milliamps per square centimeter in a range of 2.5 to 4.0 volts at 23°C. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 18.9mg

of the  $\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$  active material prepared by the method of the invention.

5 **Figure 11** shows the results of an x-ray diffraction analysis of the gamma- $\text{Li}_x\text{V}_2\text{O}_5$  ( $x = 1$ , gamma  $\text{LiV}_2\text{O}_5$ ) prepared according to the invention using  $\text{CuK}\alpha$  radiation  $\lambda = 1.5405\text{\AA}$ . The values are  $a = 9.687\text{\AA}$  (1),  $b = 3.603\text{\AA}$  (2), and  $c = 10.677\text{\AA}$  (3); phase type is gamma- $\text{Li}_x\text{V}_2\text{O}_5$  ( $x = 1$ ); symmetry is orthorhombic; and space group is Pnma.

10 **Figure 12** is a voltage/capacity plot of gamma- $\text{LiV}_2\text{O}_5$ -containing cathode cycled with a lithium metal anode using constant current cycling at  $\pm 0.2$  milliamps per square centimeter in a range of 2.5 to 3.8 volts at  $23^\circ\text{C}$ . Other conditions are as described earlier with  
15 respect to **Figure 2**. The cathode contained 21mg of the gamma- $\text{LiV}_2\text{O}_5$  active material prepared by the method of the invention.

**Figure 13** is a two-part graph based on multiple constant current cycling of gamma- $\text{LiV}_2\text{O}_5$  cycled with a  
20 lithium metal anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at  $\pm 0.2$  milliamps per square centimeter, 2.5 to 3.8 volts. In the two-part graph, **Figure 13** shows the excellent rechargeability of the lithium-metal-  
25 oxide/lithium metal cell. **Figure 13** shows the excellent cycling and capacity of the cell.

**Figure 14** shows the results of an x-ray diffraction analysis of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  prepared according to the invention. The analysis is based on  $\text{CuK}\alpha$

WO 01/53198

PCT/US00/35438

21.

radiation,  $\lambda = 1.5405\text{\AA}$ . The values are  $a = 12.184\text{\AA}$  (2),  $b = 8.679\text{\AA}$  (2),  $c = 8.627\text{\AA}$  (3), and  $\beta = 90.457^\circ$  (4).

**Figure 15** shows the results of an x-ray diffraction analysis of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  prepared according to a method described in U.S. Patent No. 5,871,866. The analysis is based on  $\text{CuK}\alpha$  radiation,  $\lambda = 1.5405\text{\AA}$ . The values are  $a = 12.155\text{\AA}$  (2),  $b = 8.711\text{\AA}$  (2),  $c = 8.645\text{\AA}$  (3); the angle beta is  $90.175^\circ$  (6); symmetry is Monoclinic; and space group is  $\text{P2}_1/\text{n}$ .

**Figure 16** is an EVS (Electrochemical Voltage Spectroscopy) voltage/capacity profile for a cell with cathode material formed by the carbothermal reduction method of the invention. The cathode material is 13.8mg of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . The cell includes a lithium metal counter electrode in an electrolyte comprising ethylene carbonate (EC) and dimethyl carbonate (DMC) in a weight ratio of 2:1 and including a 1 molar concentration of  $\text{LiPF}_6$  salt. The lithium-metal-phosphate containing electrode and the lithium metal counter electrode are maintained spaced apart by a fiberglass separator which is interpenetrated by the solvent and the salt. The conditions are  $\pm 10$  mV steps, between about 3.0 and 4.2 volts, and the critical limiting current density is less than or equal to  $0.1 \text{ mA/cm}^2$ .

**Figure 17** is an EVS differential capacity versus voltage plot for the cell as described in connection with **Figure 16**.

**Figure 18** shows multiple constant current cycling of  $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$  cycled with a lithium metal anode using the electrolyte as described in connection



with **Figure 2** and cycled, charge and discharge at  $\pm 0.2$  milliamps per square centimeter, 2.5 to 4.0 volts at two different temperature conditions,  $23^{\circ}\text{C}$  and  $60^{\circ}\text{C}$ . **Figure 18** shows the excellent rechargeability of the lithium-metal-phosphate/lithium metal cell, and also shows the excellent cycling and capacity of the cell.

**Figure 19** is a graph of potential over time for the first four complete cycles of the  $\text{LiMg}_{0.1}\text{Fe}_{0.9}\text{PO}_4/\text{MCMB}$  graphite cell of the invention.

**Figure 20** is a two-part graph based on multiple constant current cycling of  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  cycled with an MCMB graphite anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at  $\pm 0.2$  milliamps per square centimeter, 2.5 to 3.6 volts,  $23^{\circ}\text{C}$  and based on a C/10 (10 hour) rate. In the two-part graph, **Figure 20** shows the excellent rechargeability of the lithium-metal-phosphate/graphite cell. **Figure 20** shows the excellent cycling and capacity of the cell.

**Figure 21** is a graph of potential over time for the first three complete cycles of the  $\gamma\text{-LiV}_2\text{O}_5/\text{MCMB}$  graphite cell of the invention.

**Figure 22** is a diagrammatic representation of a typical laminated lithium-ion battery cell structure.

**Figure 23** is a diagrammatic representation of a typical multi-cell battery cell structure.

### Detailed Description of the Preferred Embodiments

The present invention provides lithium-mixed metal-phosphates, which are usable as electrode active materials, for lithium ( $\text{Li}^+$ ) ion removal and insertion.

5 Upon extraction of the lithium ions from the lithium-mixed-metal-phosphates, significant capacity is achieved. In one aspect of the invention, electrochemical energy is provided when combined with a suitable counter electrode by extraction of a quantity  $x$  of lithium from lithium-mixed-metal-phosphates  $\text{Li}_{a-x}\text{MI}_b\text{MII}_c(\text{PO}_4)_d$ . When a quantity  $x$  of lithium is removed per formula unit of the lithium-mixed-metal phosphate, metal MI is oxidized. In another aspect, metal MII is also oxidized. Therefore, at least one of MI and MII is oxidizable from its initial  
10 condition in the phosphate compound as Li is removed. Consider the following which illustrate the mixed metal compounds of the invention:  $\text{LiFe}_{1-y}\text{Sn}_y\text{PO}_4$ , has two oxidizable elements, Fe and Sn; in contrast,  $\text{LiFe}_{1-y}\text{Mg}_y\text{PO}_4$  has one oxidizable metal, the metal Fe.

20 In another aspect, the invention provides a lithium ion battery which comprises an electrolyte; a negative electrode having an insertion active material; and a positive electrode comprising a lithium-mixed-metal-phosphate active material characterized by an ability to release lithium ions for insertion into the  
25 negative electrode active material. The lithium-mixed-metal-phosphate is desirably represented by the nominal general formula  $\text{Li}_a\text{MI}_b\text{MII}_c(\text{PO}_4)_d$ . Although the metals MI and MII may be the same, it is preferred that the metals MI and MII are different. Desirably, in the phosphate  
30 compound MI is a metal selected from the group: Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr and mixtures thereof, and MI is

most desirably a transition metal or mixture thereof selected from said group. Most preferably, MI has a +2 valence or oxidation state.

In another aspect, MII is selected from Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof. Most preferably, MII has a +2 valence or oxidation state. The lithium-mixed-metal-phosphate is preferably a compound represented by the nominal general formula  $\text{Li}_{a-x}\text{MI}_b\text{MII}_c(\text{PO}_4)_d$ , signifying the preferred composition and its capability to release x lithium. Accordingly, during cycling, charge and discharge, the value of x varies as x greater than or equal to 0 and less than or equal to a. The present invention resolves a capacity problem posed by conventional cathode active materials. Such problems with conventional active materials are described by Tarascon in U.S. Patent No. 5,425,932, using  $\text{LiMn}_2\text{O}_4$  as an example. Similar problems are observed with  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and many, if not all, lithium metal chalcogenide materials. The present invention demonstrates that significant capacity of the cathode active material is utilizable and maintained.

A preferred novel procedure for forming the lithium-mixed-metal-phosphate  $\text{Li}_a\text{MI}_b\text{MII}_c(\text{PO}_4)_d$  compound active material will now be described. In addition, the preferred novel procedure is also applicable to formation of other lithium metal compounds, and will be described as such. The basic procedure will be described with reference to exemplary starting materials but is not limited thereby. The basic process comprises conducting a reaction between a lithium compound, preferably lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), metal compound(s), for example, vanadium pentoxide ( $\text{V}_2\text{O}_5$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), and/or

manganese hydroxide, and a phosphoric acid derivative, preferably the phosphoric acid ammonium salt, diammonium hydrogen phosphate,  $(\text{NH}_4)_2\text{H}(\text{PO}_4)$ . Each of the precursor starting materials are available from a number of

5 chemical outfits including Aldrich Chemical Company and Fluka. Using the method described herein,  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ ,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  were prepared with approximately a stoichiometric amount of  $\text{Li}_2\text{CO}_3$ , the respective metal compound, and  $(\text{NH}_4)_2\text{HPO}_4$ . Carbon powder was included with

10 these precursor materials. The precursor materials were initially intimately mixed and dry ground for about 30 minutes. The intimately mixed compounds were then pressed into pellets. Reaction was conducted by heating in an oven at a preferred ramped heating rate to an

15 elevated temperature, and held at such elevated temperature for several hours to complete formation of the reaction product. The entire reaction was conducted in a non-oxidizing atmosphere, under flowing pure argon gas. The flow rate will depend upon the size of the oven

20 and the quantity needed to maintain the atmosphere. The oven was permitted to cool down at the end of the reaction period, where cooling occurred at a desired rate under argon. Exemplary and preferred ramp rates, elevated reaction temperatures and reaction times are

25 described herein. In one aspect, a ramp rate of  $2^\circ/\text{minute}$  to an elevated temperature in a range of  $750^\circ\text{C}$  to  $800^\circ\text{C}$  was suitable along with a dwell (reaction time) of 8 hours. Refer to Reactions 1, 2, 3 and 4 herein. In

30 **another variation per Reaction 5, a reaction temperature** of  $600^\circ\text{C}$  was used along with a dwell time of about one hour. In still another variation, as per Reaction 6, a two-stage heating was conducted, first to a temperature of  $300^\circ\text{C}$  and then to a temperature of  $850^\circ$ .

The general aspects of the above synthesis route are applicable to a variety of starting materials. Lithium-containing compounds include  $\text{Li}_2\text{O}$  (lithium oxide),  $\text{LiH}_2\text{PO}_4$  (lithium hydrogen phosphate),  $\text{Li}_2\text{C}_2\text{O}_4$  (lithium oxalate),  $\text{LiOH}$  (lithium hydroxide),  $\text{LiOH}\cdot\text{H}_2\text{O}$  (lithium hydroxide monohydrate), and  $\text{LiHCO}_3$  (lithium hydrogen carbonate). The metal compounds(s) are reduced in the presence of the reducing agent, carbon. The same considerations apply to other lithium-metal- and phosphate-containing precursors. The thermodynamic considerations such as ease of reduction, of the selected precursors, the reaction kinetics, and the melting point of the salts will cause adjustment in the general procedure, such as, amount of carbon reducing agent, and the temperature of reaction.

**Figures 1** through **21** which will be described more particularly below show characterization data and capacity in actual use for the cathode materials (positive electrodes) of the invention. Some tests were conducted in a cell comprising a lithium metal counter electrode (negative electrode) and other tests were conducted in cells having a carbonaceous counter electrode. All of the cells had an  $\text{EC}:\text{DMC}:\text{LiPF}_6$  electrolyte.

Typical cell configurations will now be described with reference to **Figures 22 and 23**; and such battery or cell utilizes the novel active material of the invention. Note that the preferred cell arrangement described here is illustrative and the invention is not limited thereby. Experiments are often performed, based on full and half cell arrangements, as per the following description. For test purposes, test cells are often

fabricated using lithium metal electrodes. When forming cells for use as batteries, it is preferred to use an insertion positive electrode as per the invention and a graphitic carbon negative electrode.

5           A typical laminated battery cell structure 10 is depicted in **Figure 22**. It comprises a negative electrode side 12, a positive electrode side 14, and an electrolyte/separator 16 there between. Negative electrode side 12 includes current collector 18, and  
10           positive electrode side 14 includes current collector 22. A copper collector foil 18, preferably in the form of an open mesh grid, upon which is laid a negative electrode membrane 20 comprising an insertion material such as carbon or graphite or low-voltage lithium insertion  
15           compound, dispersed in a polymeric binder matrix. An electrolyte/separator film 16 membrane is preferably a plasticized copolymer. This electrolyte/separator preferably comprises a polymeric separator and a suitable electrolyte for ion transport. The electrolyte/separator  
20           is positioned upon the electrode element and is covered with a positive electrode membrane 24 comprising a composition of a finely divided lithium insertion compound in a polymeric binder matrix. An aluminum collector foil or grid 22 completes the assembly.  
25           Protective bagging material 40 covers the cell and prevents infiltration of air and moisture.

          In another embodiment, a multi-cell battery configuration as per **Figure 23** is prepared with copper current collector 51, negative electrode 53,  
30           electrolyte/separator 55, positive electrode 57, and aluminum current collector 59. Tabs 52 and 58 of the current collector elements form respective terminals for

the battery structure. As used herein, the terms "cell" and "battery" refer to an individual cell comprising anode/electrolyte/cathode and also refer to a multi-cell arrangement in a stack.

5           The relative weight proportions of the components of the positive electrode are generally: 50-90% by weight active material; 5-30% carbon black as the electric conductive diluent; and 3-20% binder chosen to hold all particulate materials in contact with one  
10 another without degrading ionic conductivity. Stated ranges are not critical, and the amount of active material in an electrode may range from 25-95 weight percent. The negative electrode comprises about 50-95% by weight of a preferred graphite, with the balance  
15 constituted by the binder. A typical electrolyte separator film comprises approximately two parts polymer for every one part of a preferred fumed silica. The conductive solvent comprises any number of suitable solvents and salts. Desirable solvents and salts are  
20 described in U.S. Patent Nos. 5,643,695 and 5,418,091. One example is a mixture of EC:DMC:LiPF<sub>6</sub> in a weight ratio of about 60:30:10.

Solvents are selected to be used individually or in mixtures, and include dimethyl carbonate (DMC),  
25 diethylcarbonate (DEC), dipropylcarbonate (DPC), ethylmethylcarbonate (EMC), ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate, lactones, esters, glymes, sulfoxides, sulfolanes, etc. The preferred solvents are EC/DMC, EC/DEC, EC/DPC and EC/EMC.  
30 The salt content ranges from 5% to 65% by weight, preferably from 8% to 35% by weight.

Those skilled in the art will understand that any number of methods are used to form films from the casting solution using conventional meter bar or doctor blade apparatus. It is usually sufficient to air-dry the  
5 films at moderate temperature to yield self-supporting films of copolymer composition. Lamination of assembled cell structures is accomplished by conventional means by pressing between metal plates at a temperature of about 120-160°C. Subsequent to lamination, the battery cell  
10 material may be stored either with the retained plasticizer or as a dry sheet after extraction of the plasticizer with a selective low-boiling point solvent. The plasticizer extraction solvent is not critical, and methanol or ether are often used.

15 Separator membrane element 16 is generally polymeric and prepared from a composition comprising a copolymer. A preferred composition is the 75 to 92% vinylidene fluoride with 8 to 25% hexafluoropropylene copolymer (available commercially from Atochem North  
20 America as Kynar FLEX) and an organic solvent plasticizer. Such a copolymer composition is also preferred for the preparation of the electrode membrane elements, since subsequent laminate interface compatibility is ensured. The plasticizing solvent may  
25 be one of the various organic compounds commonly used as solvents for electrolyte salts, e.g., propylene carbonate or ethylene carbonate, as well as mixtures of these compounds. Higher-boiling plasticizer compounds such as dibutyl phthalate, dimethyl phthalate, diethyl phthalate,  
30 and tris butoxyethyl phosphate are particularly suitable. Inorganic filler adjuncts, such as fumed alumina or silanized fumed silica, may be used to enhance the physical strength and melt viscosity of a separator



membrane and, in some compositions, to increase the subsequent level of electrolyte solution absorption.

In the construction of a lithium-ion battery, a current collector layer of aluminum foil or grid is overlaid with a positive electrode film, or membrane, separately prepared as a coated layer of a dispersion of insertion electrode composition. This is typically an insertion compound such as  $\text{LiMn}_2\text{O}_4$  (LMO),  $\text{LiCoO}_2$ , or  $\text{LiNiO}_2$ , powder in a copolymer matrix solution, which is dried to form the positive electrode. An electrolyte/separator membrane is formed as a dried coating of a composition comprising a solution containing VdF:HFP copolymer and a plasticizer solvent is then overlaid on the positive electrode film. A negative electrode membrane formed as a dried coating of a powdered carbon or other negative electrode material dispersion in a VdF:HFP copolymer matrix solution is similarly overlaid on the separator membrane layer. A copper current collector foil or grid is laid upon the negative electrode layer to complete the cell assembly. Therefore, the VdF:HFP copolymer composition is used as a binder in all of the major cell components, positive electrode film, negative electrode film, and electrolyte/separator membrane. The assembled components are then heated under pressure to achieve heat-fusion bonding between the plasticized copolymer matrix electrode and electrolyte components, and to the collector grids, to thereby form an effective laminate of cell elements. This produces an essentially unitary and flexible battery cell structure.

Examples of forming cells containing metallic lithium anode, insertion electrodes, solid electrolytes

WO 01/53198

PCT/US00/35438

31

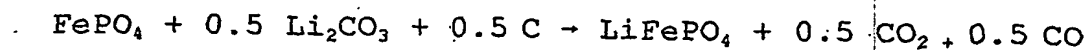
and liquid electrolytes can be found in U.S. Patent Nos. 4,668,595; 4,830,939; 4,935,317; 4,990,413; 4,792,504; 5,037,712; 5,262,253; 5,300,373; 5,435,054; 5,463,179; 5,399,447; 5,482,795 and 5,411,820; each of which is  
5 incorporated herein by reference in its entirety. Note that the older generation of cells contained organic polymeric and inorganic electrolyte matrix materials, with the polymeric being most preferred. The polyethylene oxide of 5,411,820 is an example. More  
10 modern examples are the VdF:HFP polymeric matrix. Examples of casting, lamination and formation of cells using VdF:HFP are as described in U.S. Patent Nos. 5,418,091; 5,460,904; 5,456,000; and 5,540,741; assigned to Bell Communications Research, each of which is  
15 incorporated herein by reference in its entirety.

As described earlier, the electrochemical cell operated as per the invention, may be prepared in a variety of ways. In one embodiment, the negative electrode may be metallic lithium. In more desirable  
20 embodiments, the negative electrode is an insertion active material, such as, metal oxides and graphite. When a metal oxide active material is used, the components of the electrode are the metal oxide, electrically conductive carbon, and binder, in  
25 proportions similar to that described above for the positive electrode. In a preferred embodiment, the negative electrode active material is graphite particles. For test purposes, test cells are often fabricated using lithium metal electrodes. When forming cells for use as  
30 batteries, it is preferred to use an insertion metal oxide positive electrode and a graphitic carbon negative electrode. Various methods for fabricating electrochemical cells and batteries and for forming

electrode components are described herein. The invention is not, however, limited by any particular fabrication method.

Formation of Active Materials**EXAMPLE I**

Reaction 1(a).  $\text{LiFePO}_4$  formed from  $\text{FePO}_4$



- 5 (a) Pre-mix reactants in the following proportions using ball mill. Thus,

1 mol $\text{FePO}_4$	150.82g
0.5 mol $\text{Li}_2\text{CO}_3$	36.95g
0.5 mol carbon	6.0g

- 10 (but use 100% excess carbon  $\rightarrow$  12.00g)

- (b) Pelletize powder mixture

- (c) Heat pellet to  $750^\circ\text{C}$  at a rate of  $2^\circ/\text{minute}$  in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at  $750^\circ\text{C}$  under argon.

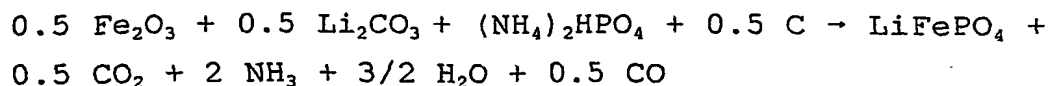
- 15 (d) Cool to room temperature at  $2^\circ/\text{minute}$  under argon.

- (e) Powderize pellet.

20 Note that at  $750^\circ\text{C}$  this is predominantly a CO reaction. This reaction is able to be conducted at a temperature in a range of about  $700^\circ\text{C}$  to about  $950^\circ\text{C}$  in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum.

**EXAMPLE II**

Reaction 1(b).  $\text{LiFePO}_4$  formed from  $\text{Fe}_2\text{O}_3$



5 (a) Premix powders in the following proportions

0.5 mol $\text{Fe}_2\text{O}_3$	79.85g
0.5 mol $\text{Li}_2\text{CO}_3$	36.95g
1 mol $(\text{NH}_4)_2\text{HPO}_4$	132.06g
0.5 mol carbon	6.00g

10 (use 100% excess carbon  $\rightarrow$  12.00g)

(b) Pelletize powder mixture

(c) Heat pellet to  $750^\circ\text{C}$  at a rate of  $2^\circ/\text{minute}$  in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at  $750^\circ\text{C}$  under argon.

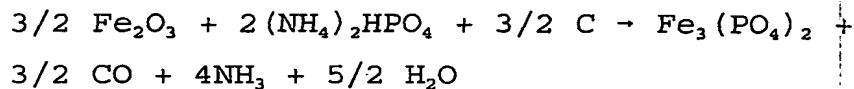
15 (d) Cool to room temperature at  $2^\circ/\text{minute}$  under argon.

(e) Powderize

**EXAMPLE III**

Reaction 1(c).  $\text{LiFePO}_4$  - from  $\text{Fe}_3(\text{PO}_4)_2$

20 Two steps:

Part I. Carbothermal preparation of  $\text{Fe}_3(\text{PO}_4)_2$ 

(a) Premix reactants in the following proportions

5	3/2 mol $\text{Fe}_2\text{O}_3$	239.54g
	2 mol $(\text{NH}_4)_2\text{HPO}_4$	264.12g
	3/2 mol carbon	18.00g

(use 100% excess carbon  $\rightarrow$  36.00g)

(b) Pelletize powder mixture

10 (c) Heat pellet to 800°C at a rate of 2°/minute in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at 750°C under argon.

(d) Cool to room temperature at 2°C/minute under argon.

15 (e) Powderize pellet.

Part II. Preparation of  $\text{LiFePO}_4$  from the  $\text{Fe}_3(\text{PO}_4)_2$  of Part I.

(a) Premix reactants in the following proportions

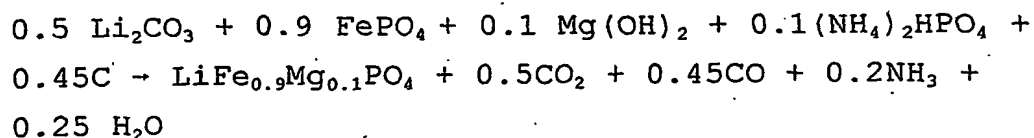
20	1 mol $\text{Li}_3\text{PO}_4$	115.79g
	1 mol $\text{Fe}_3(\text{PO}_4)_2$	357.48g

(b) Pelletize powder mixture

- (c) Heat pellet to 750°C at a rate of 2°/minute in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at 750°C under argon.
- (d) Cool to room temperature at 2°C/minute under argon.
- (e) Powderize pellet.

**EXAMPLE IV**

Reaction 2(a).  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  ( $\text{LiFe}_{1-y}\text{Mg}_y\text{PO}_4$ ) formed from  $\text{FePO}_4$



- (a) Pre-mix reactants in the following proportions

0.50 mol $\text{Li}_2\text{CO}_3$	=	36.95g
0.90 mol $\text{FePO}_4$	=	135.74g
0.10 mol $\text{Mg(OH)}_2$	=	5.83g
0.10 mol $(\text{NH}_4)_2\text{HPO}_4$	=	1.32g
0.45 mol carbon	=	5.40g

(use 100% excess carbon - 10.80g)

- (b) Pelletize powder mixture
- (c) Heat to 750°C at a rate of 2°/minute in argon. Hold for 8 hours dwell at 750°C in argon
- (d) Cool at a rate of 2°/minute

WO 01/53198

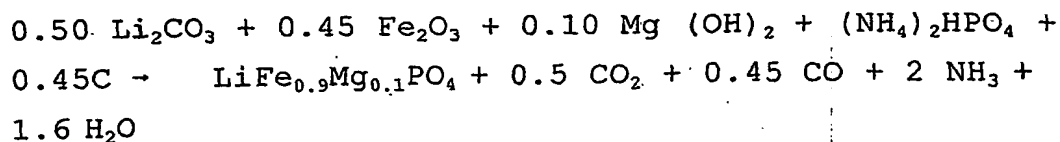
PCT/US00/35438

37

(e) Powderize pellet.

**EXAMPLE V**

Reaction 2(b).  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  ( $\text{LiFe}_{1-y}\text{Mg}_y\text{PO}_4$ ) formed from  
5  $\text{Fe}_2\text{O}_3$



10 (a) Pre-mix reactants in following ratio

	0.50 mol $\text{Li}_2\text{CO}_3$	=	36.95g
	0.45 mol $\text{Fe}_2\text{O}_3$	=	71.86g
	0.10 mol $\text{Mg (OH)}_2$	=	5.83g
	1.00 mol $(\text{NH}_4)_2\text{HPO}_4$	=	132.06g
15	0.45 mol carbon	=	5.40g

(use 100% excess carbon  $\rightarrow$  10.80g)

(b) Pelletize powder mixture

(c) Heat to  $750^\circ\text{C}$  at a rate of  $2^\circ/\text{minute}$  in argon.  
Hold for 8 hours dwell at  $750^\circ\text{C}$  in argon

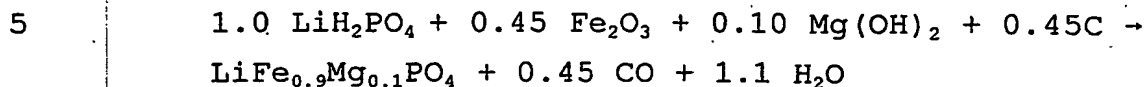
20 (d) Cool at a rate of  $2^\circ/\text{minute}$

(e) Powderize pellet.



**EXAMPLE VI**

Reaction 2(c).  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  ( $\text{LiFe}_{1-y}\text{Mg}_y\text{PO}_4$ ) formed from  $\text{LiH}_2\text{PO}_4$



(a) Pre-mix reactants in the following proportions

	1.00 mol $\text{LiH}_2\text{PO}_4$	=	103.93g
	0.45 mol $\text{Fe}_2\text{O}_3$	=	71.86g
10	0.10 mol $\text{Mg(OH)}_2$	=	5.83g
	0.45 mol carbon	=	5.40g

(use 100% excess carbon  $\rightarrow$  10.80g)

(b) Pelletize powder mixture

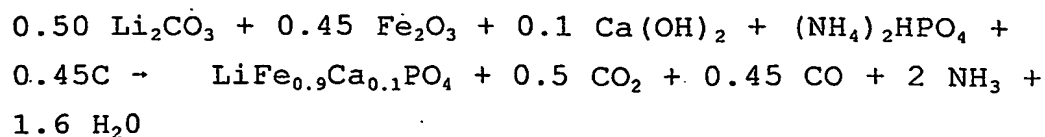
15            (c) Heat to  $750^\circ\text{C}$  at a rate of  $2^\circ/\text{minute}$  in argon.  
              Hold for 8 hours dwell at  $750^\circ\text{C}$  in argon

(d) Cool at a rate of  $2^\circ/\text{minute}$

(e) Powderize pellet.

**EXAMPLE VII**

20            Reaction 3.      Formation of  $\text{LiFe}_{0.9}\text{Ca}_{0.1}\text{PO}_4$   
              ( $\text{LiFe}_{1-y}\text{Ca}_y\text{PO}_4$ ) from  $\text{Fe}_2\text{O}_3$



WO 01/53198

PCT/US00/35438

39

(a) Pre-mix reactants in the following proportions

	0.50 mol $\text{Li}_2\text{CO}_3$	=	36.95g
	0.45 mol $\text{Fe}_2\text{O}_3$	=	71.86g
	0.10 mol $\text{Ca}(\text{OH})_2$	=	7.41g
5	1.00 mol $(\text{NH}_4)_2\text{HPO}_4$	=	132.06g
	0.45 mol carbon	=	5.40g

(100% excess carbon → 10.80g)

(b) Pelletize powder mixture

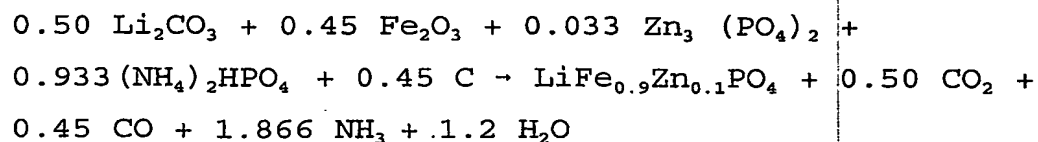
10 (c) Heat to 750°C at a rate of 2°/minute in argon.  
Hold for 8 hours dwell at 750°C in argon

(d) Cool at a rate of 2°/minute

(e) Powderize pellet.

**EXAMPLE VIII**

15 Reaction 4. Formation of  $\text{LiFe}_{0.9}\text{Zn}_{0.1}\text{PO}_4$   
( $\text{LiFe}_{1-y}\text{Zn}_y\text{PO}_4$ ) from  $\text{Fe}_2\text{O}_3$ .



20 Pre-mix reactants in the following proportions

	0.50 mol $\text{Li}_2\text{CO}_3$	=	36.95g
	0.45 mol $\text{Fe}_2\text{O}_3$	=	71.86g
	0.033 mol $\text{Zn}_3(\text{PO}_4)_2$	=	12.74g

40

0.45 mol carbon = 5.40g

(100% excess carbon - 10.80g)

(b) Pelletize powder mixture

5 (c) Heat to 750°C at a rate of 2°/minute in argon.  
Hold for 8 hours dwell at 750°C in argon

(d) Cool at a rate of 2°/minute

(e) Powderize pellet.

#### EXAMPLE IX

Reaction 5. Formation of gamma-LiV<sub>2</sub>O<sub>5</sub> (γ)

10 
$$\text{V}_2\text{O}_5 + 0.5 \text{Li}_2\text{CO}_3 + 0.25 \text{C} \rightarrow \text{LiV}_2\text{O}_5 + 3/4 \text{CO}_2$$

(a) Pre-mix alpha V<sub>2</sub>O<sub>5</sub>, Li<sub>2</sub>CO<sub>3</sub> and Shiwinigan Black (carbon) using ball mix with suitable media. Use a 25% weight excess of carbon over the reaction amounts above. For example, according to reaction above:

15

Need:	1 mol V <sub>2</sub> O <sub>5</sub>	181.88g
	0.5 mol Li <sub>2</sub> CO <sub>3</sub>	36.95g
	0.25 mol carbon	3.00g

(but use 25% excess carbon - 3.75g)

WO 01/53198

PCT/US00/35438

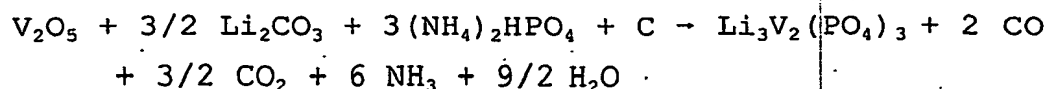
41

- (b) Pelletize powder mixture
- (c) Heat pellet to 600°C in flowing argon (or other inert atmosphere) at a heat rate of approximately 2°/minute. Hold at 600°C for about 60 minutes.
- (d) Allow to cool to room temperature in argon at cooling rate of about 2°/minute.
- (e) Powderize pellet using mortar and pestle

This reaction is able to be conducted at a temperature in a range of about 400°C to about 650°C in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum. This reaction at this temperature range is primarily  $C \rightarrow CO_2$ . Note that the reaction  $C \rightarrow CO$  primarily occurs at a temperature over about 650°C (HT, high temperature); and the reaction  $C \rightarrow CO_2$  primarily occurs at a temperature of under about 650°C (LT, low temperature). The reference to about 650°C is approximate and the designation "primarily" refers to the predominant reaction thermodynamically favored although the alternate reaction may occur to some extent.

**EXAMPLE X**

Reaction 6. Formation of  $Li_3V_2(PO_4)_3$



- (a) Pre-mix reactants above using ball mill with suitable media. Use a 25% weight excess of carbon. Thus,

5	1 mol $V_2O_5$	181.88g
	$3/2$ mol $Li_2CO_3$	110.84g
	3 mol $(NH_4)_2HPO_4$	396.18g
	1 mol carbon	12.01g

(but use 25% excess carbon  $\rightarrow$  15.01g)

- (b) Pelletize powder mixture
- 10 (c) Heat pellet at  $2^\circ/\text{minute}$  to  $300^\circ\text{C}$  to remove  $CO_2$  (from  $Li_2CO_3$ ) and to remove  $NH_3$ ,  $H_2O$ . Heat in an inert atmosphere (e.g. argon). Cool to room temperature.
- (d) Powderize and repelletize
- 15 (e) Heat pellet in inert atmosphere at a rate of  $2^\circ/\text{minute}$  to  $850^\circ\text{C}$ . Dwell for 8 hours at  $850^\circ\text{C}$
- (f) Cool to room temperature at a rate of  $2^\circ/\text{minute}$  in argon.
- 20 (e) Powderize

This reaction is able to be conducted at a temperature in a range of about  $700^\circ\text{C}$  to about  $950^\circ\text{C}$  in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum. A reaction temperature greater than about  $670^\circ\text{C}$  ensures  $C \rightarrow CO$  reaction is primarily carried out.

25

**Characterization of Active Materials  
and Formation and Testing of Cells**

Referring to **Figure 1**, the final product  $\text{LiFePO}_4$ , prepared from  $\text{Fe}_2\text{O}_3$  metal compound per Reaction 1(b), appeared brown/black in color. This olivine material product included carbon that remained after reaction. Its  $\text{CuK}\alpha$  x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 1**. The pattern evident in **Figure 1** is consistent with the single phase olivine phosphate,  $\text{LiFePO}_4$ . This is evidenced by the position of the peaks in terms of the scattering angle  $2\theta$  (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Here the space group  $\text{SG} = \text{pnma}$  (62) and the lattice parameters from XRD refinement are consistent with the olivine structure. The values are  $a = 10.2883\text{\AA}$  (0.0020),  $b = 5.9759$  (0.0037),  $c = 4.6717\text{\AA}$  (0.0012) 0.0072, cell volume =  $287.2264\text{\AA}^3$  (0.0685). Density,  $\rho = 3.605$  g/cc, zero = 0.452 (0.003). Peak at full width half maximum, PFWHM = 0.21. Crystallite size from XRD data =  $704\text{\AA}$ .

The x-ray pattern demonstrates that the product of the invention was indeed the nominal formula  $\text{LiFePO}_4$ . The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent, and that some portion of P may be substituted by Si, S or As; and some portion of O may be substituted by halogen, preferably F.

The  $\text{LiFePO}_4$ , prepared as described immediately above, was tested in an electrochemical cell. The positive electrode was prepared as described above, using 19.0mg of active material. The positive electrode  
5 contained, on a weight % basis, 85% active material, 10% carbon black, and 5% EPDM. The negative electrode was metallic lithium. The electrolyte was a 2:1 weight ratio mixture of ethylene carbonate and dimethyl carbonate within which was dissolved 1 molar  $\text{LiPF}_6$ . The cells were  
10 cycled between about 2.5 and about 4.0 volts with performance as shown in **Figures 2 and 3**.

**Figure 2** shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon  
15 about 19 milligrams of the  $\text{LiFePO}_4$  active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is  $\text{LiFePO}_4$ . The lithium is extracted from the  $\text{LiFePO}_4$  during charging of the cell. When fully  
20 charged, about 0.72 unit of lithium had been removed per formula unit. Consequently, the positive electrode active material corresponds to  $\text{Li}_{1-x}\text{FePO}_4$  where  $x$  appears to be equal to about 0.72, when the cathode material is at 4.0 volts versus  $\text{Li/Li}^+$ . The extraction represents  
25 approximately 123 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 19 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the  $\text{LiFePO}_4$ . The re-insertion corresponds to approximately 121 milliamp  
30 hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total

cumulative capacity demonstrated during the entire extraction-insertion cycle is 244mAh/g.

5       **Figure 3** presents data obtained by multiple constant current cycling at 0.2 milliamp hours per square centimeter of the  $\text{LiFePO}_4$  versus lithium metal counter electrode between 2.5 and 4.0 volts. Data is shown for two temperatures, 23°C and 60°C. **Figure 3** shows the excellent rechargeability of the  $\text{LiFePO}_4$  cell, and also shows good cycling and capacity of the cell. The  
10       performance shown after about 190 to 200 cycles is good and shows that electrode formulation is very desirable.

Referring to **Figure 4**, there is shown data for the final product  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ , prepared from the metal compounds  $\text{Fe}_2\text{O}_3$  and  $\text{Mg}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2$ , per Reaction 2(b).  
15       Its  $\text{CuK}\alpha$  x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 4**. The pattern evident in **Figure 4** is consistent with the single phase olivine phosphate compound,  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ . This is evidenced by the position of the peaks in terms  
20       of the scattering angle  $2\theta$  (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Here the space group SG = Pnma (62) and the lattice parameters from XRD  
25       refinement are consistent with the olivine structure. The values are  $a = 10.2688\text{\AA}$  (0.0069),  $b = 5.9709\text{\AA}$  (0.0072),  $c = 4.6762\text{\AA}$  (0.0054), cell volume =  $286.7208\text{\AA}^3$  (0.04294),  $\rho = 3.617$  g/cc, zero = 0.702 (0.003), PFWHM = 0.01, and crystallite =  $950\text{\AA}$ .



LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub>. The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent, and that some substitution of P and O may be made while maintaining the basic olivine structure.

The LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub>, prepared as described immediately above, was tested in an electrochemical cell. The positive electrode was prepared as described above, using 18.9mg of active materials. The positive electrode, negative electrode and electrolyte were prepared as described earlier and in connection with Figure 1. The cell was between about 2.5 and about 4.0 volts with performance as shown in Figures 4, 5 and 6.

Figure 5 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.9 milligrams of the LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub> active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub>. The lithium is extracted from the LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub> during charging of the cell. When fully charged, about 0.87 units of lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to Li<sub>1-x</sub>Fe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub> where x appears to be equal to about 0.87, when the cathode material is at 4.0 volts versus Li/Li<sup>+</sup>. The extraction represents approximately 150 milliamp hours per gram corresponding to about 2.8 milliamp hours based on 18.9 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub>. The re-

insertion corresponds to approximately 146 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total cumulative specific capacity over the entire cycle is 296 mAh/g. This material has a much better cycle profile than the  $\text{LiFePO}_4$ . **Figure 5** ( $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ ) shows a very well defined and sharp peak at about 150 mAh/g. In contrast, **Figure 2** ( $\text{LiFePO}_4$ ) shows a very shallow slope leading to the peak at about 123 mAh/g. The Fe-phosphate (**Figure 2**) provides 123 mAh/g compared to its theoretical capacity of 170 mAh/g. This ratio of 123/170, 72% is relatively poor compared to the Fe/Mg-phosphate. The Fe/Mg-phosphate (**Figure 5**) provides 150 mAh/g compared to a theoretical capacity of 160, a ratio of 150/160 or 94%.

**Figure 6** presents data obtained by multiple constant current cycling at 0.2 milliamp hours per square centimeter of the  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  versus lithium metal counter electrode between 2.5 and 4.0 volts. **Figure 6** shows the excellent rechargeability of the  $\text{Li}/\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  cell, and also shows good cycling and capacity of the cell. The performance shown after about 150 to 160 cycles is very good and shows that electrode formulation  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  performed significantly better than the  $\text{LiFePO}_4$ . Comparing **Figure 3** ( $\text{LiFePO}_4$ ) to **Figure 6** ( $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ ) it can be seen that the Fe/Mg-phosphate maintains its capacity over prolonged cycling, whereas the Fe-phosphate capacity fades significantly.

**Figure 7** shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 16 milligrams of the  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  active material

in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is  $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ . The lithium is extracted from the  $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$  during charging of the cell. When fully charged, about 0.79 units of lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to  $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$  where x appears to be equal to about 0.79, when the cathode material is at 4.0 volts versus  $\text{Li}/\text{Li}^+$ . The extraction approximately 140 milliamp hours per gram corresponding to about 2.2 milliamp hours based on 16 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the  $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ . The re-insertion corresponds to approximately 122 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total cumulative specific capacity over the entire cycle is 262 mAh/g.

Referring to **Figure 8**, there is shown data for the final product  $\text{LiFe}_{0.9}\text{Ca}_{0.1}\text{PO}_4$ , prepared from  $\text{Fe}_2\text{O}_3$  and  $\text{Ca}(\text{OH})_2$  by Reaction 3. Its  $\text{CuK}\alpha$  x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 8**. The pattern evident in **Figure 8** is consistent with the single phase olivine phosphate compound,  $\text{LiFe}_{0.9}\text{Ca}_{0.1}\text{PO}_4$ . This is evidenced by the position of the peaks in terms of the scattering angle  $2\theta$  (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Here the space group  $\text{SG} = \text{Pnma}$  (62) and the lattice parameters from XRD refinement are consistent with olivine. The values are  $a = 10.3240\text{\AA}$  (0.0045),  $b =$

6.0042Å (0.0031),  $c = 4.6887\text{\AA}$  (0.0020), cell volume =  
290.6370Å (0.1807), zero = 0.702 (0.003),  $\rho = 3.62\text{ g/cc}$ ,  
FWHM = 0.18, and crystallite = 680Å. The x-ray pattern  
demonstrates that the product of the invention was indeed  
5 the nominal formula  $\text{LiFe}_{0.9}\text{Ca}_{0.1}\text{PO}_4$ .

Figure 9 shows the results of the first  
constant current cycling at 0.2 milliamps per square  
centimeter between about 2.5 and 4.0 volts based upon  
about 18.5 milligrams of the  $\text{LiFe}_{0.8}\text{Ca}_{0.2}\text{PO}_4$  active  
10 material in the cathode (positive electrode). In an as  
prepared, as assembled, initial condition, the positive  
electrode active material is  $\text{LiFe}_{0.8}\text{Ca}_{0.2}\text{PO}_4$ . The lithium  
is extracted from the  $\text{LiFe}_{0.8}\text{Ca}_{0.2}\text{PO}_4$  during charging of  
the cell. When fully charged, about 0.71 units of  
15 lithium have been removed per formula unit.  
Consequently, the positive electrode active material  
corresponds to  $\text{LiFe}_{0.8}\text{Ca}_{0.2}\text{PO}_4$  where  $x$  appears to be equal  
to about 0.71, when the cathode material is at 4.0 volts  
versus  $\text{Li/Li}^+$ . The extraction represents approximately  
20 123 milliamp hours per gram corresponding to about 2.3  
milliamp hours based on 18.5 milligrams active material.  
Next, the cell is discharged whereupon a quantity of  
lithium is re-inserted into the  $\text{LiFe}_{0.8}\text{Ca}_{0.2}\text{PO}_4$ . The re-  
insertion corresponds to approximately 110 milliamp hours  
25 per gram proportional to the insertion of nearly all of  
the lithium. The bottom of the curve corresponds to  
approximately 2.5 volts. The total specific cumulative  
capacity over the entire cycle is 233 mAh/g.

Figure 10 shows the results of the first  
30 constant current cycling at 0.2 milliamps per square  
centimeter between about 2.5 and 4.0 volts based upon  
about 18.9 milligrams of the  $\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$  olivine active

material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is  $\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$ , prepared from  $\text{Fe}_2\text{O}_3$  and  $\text{Zn}_3(\text{PO}_4)_2$  by Reaction 4. The lithium is  
 5 extracted from the  $\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$  during charging of the cell. When fully charged, about 0.74 units of lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to  $\text{Li}_{1-x}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$  where  $x$  appears to be equal to about 0.74,  
 10 when the cathode material is at 4.0 volts versus  $\text{Li}/\text{Li}^+$ . The extraction represents approximately 124 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 18.9 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-  
 15 inserted into the  $\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$ . The re-insertion corresponds to approximately 108 milliamp hours per gram proportional to the insertion of nearly all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts.

20 Referring to **Figure 11**, the final product  $\text{LiV}_2\text{O}_5$ , prepared by Reaction 5, appeared black in color. Its  $\text{CuK}\alpha$  x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 11**. The pattern evident in **Figure 11** is consistent with a  
 25 single oxide compound gamma- $\text{LiV}_2\text{O}_5$ . This is evidenced by the position of the peaks in terms of the scattering angle  $2\theta$  (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely  
 30 completed.

The x-ray pattern demonstrates that the product of the invention was indeed the nominal formula gamma-

$\text{LiV}_2\text{O}_5$ . The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent.

5           The  $\text{LiV}_2\text{O}_5$  prepared as described immediately above, was tested in an electrochemical cell. The cell was prepared as described above and cycled with performance as shown in **Figures 12 and 13**.

**Figure 12** shows the results of the first  
10   constant current cycling at 0.2 milliamps per square centimeter between about 2.8 and 3.8 volts based upon about 15.0 milligrams of the  $\text{LiV}_2\text{O}_5$  active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode  
15   active material is  $\text{LiV}_2\text{O}_5$ . The lithium is extracted from the  $\text{LiV}_2\text{O}_5$  during charging of the cell. When fully charged, about 0.93 unit of lithium had been removed per formula unit. Consequently, the positive electrode active material corresponds to  $\text{Li}_{1-x}\text{V}_2\text{O}_5$  where x appears to  
20   be equal to about 0.93, when the cathode material is at 3.8 volts versus  $\text{Li}/\text{Li}^+$ . The extraction represents approximately 132 milliamp hours per gram corresponding to about 2.0 milliamp hours based on 15.0 milligrams active material. Next, the cell is discharged whereupon  
25   a quantity of lithium is re-inserted into the  $\text{LiV}_2\text{O}_5$ . The re-insertion corresponds to approximately 130 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.8 volts.

30           **Figure 13** presents data obtained by multiple constant current cycling at 0.4 milliamp hours per square

centimeter (C/2 rate) of the  $\text{LiV}_2\text{O}_5$  versus lithium metal counter electrode between 3.0 and 3.75 volts. Data for two temperature conditions are shown, 23°C and 60°C.

5 **Figure 13** is a two part graph with **Figure 13A** showing the excellent rechargeability of the  $\text{LiV}_2\text{O}_5$ . **Figure 13B** shows good cycling and capacity of the cell. The performance shown up to about 300 cycles is good.

Referring to **Figure 14**, the final product  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , prepared by Reaction 6, appeared green/black  
10 in color. Its  $\text{CuK}\alpha$  x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 14**. The pattern evident in **Figure 14** is consistent with a single phosphate compound  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  of the monoclinic, Nasicon phase. This is evidenced by the  
15 position of the peaks in terms of the scattering angle  $2\theta$  (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed.

The x-ray pattern demonstrates that the product  
20 of the invention was indeed the nominal formula  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent; and that substitution  
25 of P and O may occur.

The  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , prepared as described immediately above, was tested in an electrochemical cell. The cell was prepared as described above, using 13.8mg of active material. The cell was prepared as described above and  
30 cycled between about 3.0 and about 4.2 volts using the EVS technique with performance as shown in **Figures 16** and

17. **Figure 16** shows specific capacity versus electrode potential against Li. **Figure 17** shows differential capacity versus electrode potential against Li.

A comparative method was used to form  
5  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . Such method was reaction without carbon and under  $\text{H}_2$ -reducing gas as described in U.S. Patent No. 5,871,866. The final product, prepared as per U.S. Patent No. 5,871,866, appeared green in color. Its  $\text{CuK}\alpha$  x-ray diffraction pattern contained all of the peaks  
10 expected for this material as shown in **Figure 15**. The pattern evident in **Figure 15** is consistent with a monoclinic Nasicon single phase phosphate compound  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . This is evidenced by the position of the peaks in terms of the scattering angle  $2\theta$  (theta), x  
15 axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Chemical analysis for lithium and vanadium by atomic absorption spectroscopy showed, on a percent by weight  
20 basis, 5.17 percent lithium and 26 percent vanadium. This is close to the expected result of 5.11 percent lithium and 25 percent vanadium.

The chemical analysis and x-ray patterns of  
25 **Figures 14 and 15** demonstrate that the product of **Figure 14** was the same as that of **Figure 15**. The product of **Figure 14** was prepared without the undesirable  $\text{H}_2$  atmosphere and was prepared by the novel carbothermal solid state synthesis of the invention.

**Figure 16** shows a voltage profile of the test  
30 cell, based on the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  positive electrode active material made by the process of the invention and as



characterized in **Figure 14**. It was cycled against a lithium metal counter electrode. The data shown in **Figure 16** is based on the Electrochemical Voltage Spectroscopy (EVS) technique. Electrochemical and kinetic data were recorded using the Electrochemical Voltage Spectroscopy (EVS) technique. Such technique is known in the art as described by J. Barker in Synth, Met 28, D217 (1989); Synth. Met. 32, 43 (1989); J. Power Sources, 52, 185 (1994); and Electrochimica Acta, Vol. 40, No. 11, at 1603 (1995). **Figure 16** clearly shows and highlights the reversibility of the product. The positive electrode contained about 13.8 milligrams of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  active material. The positive electrode showed a performance of about 133 milliamp hours per gram on the first discharge. In **Figure 16**, the capacity in, and the capacity out are essentially the same, resulting in essentially no capacity loss. **Figure 17** is an EVS differential capacity plot based on **Figure 16**. As can be seen from **Figure 17**, the relatively symmetrical nature of peaks indicates good electrical reversibility, there are small peak separations (charge/discharge), and good correspondence between peaks above and below the zero axis. There are essentially no peaks that can be related to irreversible reactions, since all peaks above the axis (cell charge) have corresponding peaks below the axis (cell discharge), and there is essentially no separation between the peaks above and below the axis. This shows that the carbothermal method of the invention produces high quality electrode material.

**Figure 18** presents data obtained by multiple constant current cycling at 0.2 milliamp hours per square centimeter of the  $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$  versus lithium metal counter electrode between 2.5 and 4.0 volts. **Figure 18**

shows the excellent rechargeability of the Li/LiFe<sub>0.8</sub>Mg<sub>0.2</sub>PO<sub>4</sub> cell, and also shows good cycling and capacity of the cell. The performance shown after about 110 to 120 cycles at 23°C is very good and shows that electrode formulation LiFe<sub>0.8</sub>Mg<sub>0.2</sub>PO<sub>4</sub> performed significantly better than the LiFePO<sub>4</sub>. The cell cycling test at 60°C was started after the 23°C test and was ongoing. Comparing **Figure 3** (LiFePO<sub>4</sub>) to **Figure 18** (LiFe<sub>0.8</sub>Mg<sub>0.2</sub>PO<sub>4</sub>), it can be seen that the Fe/Mg-phosphate maintains its capacity over prolonged cycling, whereas the Fe-phosphate capacity fades significantly.

In addition to the above cell tests, the active materials of the invention were also cycled against insertion anodes in non-metallic, lithium ion, rocking chair cells.

The lithium mixed metal phosphate and the lithium metal oxide were used to formulate a cathode electrode. The electrode was fabricated by solvent casting a slurry of the treated, enriched lithium manganese oxide, conductive carbon, binder, plasticizer and solvent. The conductive carbon used was Super P (MMM Carbon). Kynar Flex 2801® was used as the binder and electronic grade acetone was used as a solvent. The preferred plasticizer was dibutyl phthalate (DPB). The slurry was cast onto glass and a free-standing electrode was formed as the solvent was evaporated. In this example, the cathode had 23.1mg LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub> active material. Thus, the proportions are as follows on a percent weight basis: 80% active material; 8% Super P carbon; and 12% Kynar binder.

A graphite counter electrode was prepared for use with the aforesaid cathode. The graphite counter electrode served as the anode in the electrochemical cell. The anode had 10.8 mg of the MCMB graphite active material. The graphite electrode was fabricated by solvent casting a slurry of MCMB2528 graphite, binder, and casting solvent. MCMB2528 is a mesocarbon microbead material supplied by Alumina Trading, which is the U.S. distributor for the supplier, Osaka Gas Company of Japan. This material has a density of about 2.24 grams per cubic centimeter; a particle size maximum for at least 95% by weight of the particles of 37 microns; median size of about 22.5 microns and an interlayer distance of about 0.336. As in the case of the cathode, the binder was a copolymer of polyvinylidene difluoride (PVdF) and hexafluoropropylene (HFP) in a wt. ratio of PVdF to HFP of 88:12. This binder is sold under the designation of Kynar Flex 2801®, showing it's a registered trademark. Kynar Flex is available from Atochem Corporation. An electronic grade solvent was used. The slurry was cast onto glass and a free standing electrode was formed as the casting solvent evaporated. The electrode composition was approximately as follows on a dry weight basis: 85% graphite; 12% binder; and 3% conductive carbon.

A rocking chair battery was prepared comprising the anode, the cathode, and an electrolyte. The ratio of the active cathode mass to the active anode mass was about 2.14:1. The two electrode layers were arranged with an electrolyte layer in between, and the layers were laminated together using heat and pressure as per the Bell Comm. Res. patents incorporated herein by reference earlier. In a preferred method, the cell is activated

with EC/DMC solvent in a weight ratio of 2:1 in a solution containing 1 M  $\text{LiPF}_6$  salt.

Figures 19 and 20 show data for the first four complete cycles of the lithium ion cell having the  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  cathode and the MCMB2528 anode. The cell comprised 23.1mg active  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  and 10.8mg active MCMB2528 for a cathode to anode mass ratio of 2.14. The cell was charged and discharged at 23°C at an approximate C/10 (10 hour) rate between voltage limits of 2.50 V and 3.60 V. The voltage profile plot (Figure 19) shows the variation in cell voltage versus time for the  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ /MCMB2528 lithium ion cell. The symmetrical nature of the charge-discharge is clearly evident. The small degree of voltage hysteresis between the charge and discharge processes is evidence for the low overvoltage in the system, which is very good. Figure 20 shows the variation of  $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$  specific capacity with cycle number. Clearly, over the cycles shown, the material demonstrates good cycling stability.

Figure 21 shows data for the first three complete cycles of the lithium ion cell having the gamma- $\text{LiV}_2\text{O}_5$  cathode and the MCMB2528 anode. The cell prepared was a rocking chair, lithium ion cell as described above. The cell comprised 29.1mg gamma- $\text{LiV}_2\text{O}_5$  cathode active material and 12.2mg MCMB2528 anode active material, for a cathode to anode mass ratio of 2.39. As stated earlier, the liquid electrolyte used was EC/DMC (2:1) and 1M  $\text{LiPF}_6$ . The cell was charged and discharged at 23°C at an approximate C/10 (10 hour) rate between voltage limits of 2.50 V and 3.65 V. The voltage profile plot (Figure 21) shows the variation in cell voltage versus time for the  $\text{LiV}_2\text{O}_5$ /MCMB2528 lithium ion cell. The symmetrical nature

of the charge-discharge is clearly evident. The small degree of voltage hysteresis between the charge and discharge processes is evidence for the low overvoltage in the system, which is very good.

5

In summary, the invention provides new compounds  $\text{Li}_x\text{MI}_y\text{MII}_z(\text{PO}_4)_d$  and  $\gamma\text{-LiV}_2\text{O}_5$  by new methods which are adaptable to commercial scale production. The  $\text{Li}_x\text{MI}_{1-y}\text{MII}_y\text{PO}_4$  compounds are isostructural olivine compounds as demonstrated by XRD analysis. Substituted compounds, such as  $\text{LiFe}_{1-y}\text{Mg}_y\text{PO}_4$  show better performance than  $\text{LiFePO}_4$  unsubstituted compounds when used as electrode active materials. The method of the invention utilizes the reducing capabilities of carbon along with selected precursors and reaction conditions to produce high quality products suitable as electrode active materials or as ion conductors. The reduction capability of carbon over a broad temperature range is selectively applied along with thermodynamic and kinetic considerations to provide an energy-efficient, economical and convenient process to produce compounds of a desired composition and structure. This is in contrast to known methods.

Principles of carbothermal reduction have been applied to produce pure metal from metal oxides by removal of oxygen. See, for example, U.S. Patent Nos. 2,580,878, 2,570,232, 4,177,060, and 5,803,974. Principles of carbothermal and thermal reduction have also been used to form carbides. See, for example, U.S. Patent Nos. 3,865,745 and 5,384,291; and non-oxide ceramics (see U.S. Patent No. 5,607,297). Such methods are not known to have been applied to form lithiated products or to form products without oxygen abstraction

from the precursor. The methods described with respect to the present invention provide high quality products which are prepared from precursors which are lithiated during the reaction without oxygen abstraction. This is a  
5 surprising result. The new methods of the invention also provide new compounds not known to have been made before.

For example,  $\alpha\text{-V}_2\text{O}_5$  is conventionally lithiated electrochemically against metallic lithium. Thus,  $\alpha\text{-V}_2\text{O}_5$  is not suitable as a source of lithium  
10 for a cell. As a result,  $\alpha\text{-V}_2\text{O}_5$  is not used in an ion cell. In the present invention,  $\alpha\text{-V}_2\text{O}_5$  is lithiated by carbothermal reduction using a simple lithium-containing compound and the reducing capability of carbon to form a  $\gamma\text{-LiV}_2\text{O}_5$ . The single phase  
15 compound,  $\gamma\text{-LiV}_2\text{O}_5$  is not known to have been directly and independently prepared before. There is not known to be a direct synthesis route. Attempts to form it as a single phase resulted in a mixed phase product containing one or more beta phases and having the formula  $\text{Li}_x\text{V}_2\text{O}_5$   
20 with  $0 < x \leq 0.49$ . This is far different from the present single phase  $\gamma\text{-Li}_x\text{V}_2\text{O}_5$  with  $x$  equal to one, or very close to one. The flexibility of the process of the present invention is such that it can be conducted over a wide temperature range. The higher the temperature, the  
25 more quickly the reaction proceeds. For example, at  $650^\circ\text{C}$ , conversion of  $\alpha\text{-V}_2\text{O}_5$  to  $\gamma\text{-LiV}_2\text{O}_5$  occurs in about one hour, and at  $500^\circ$  it takes about 8 hours. Here, about one quarter ( $1/4$ ) atomic unit of carbon is used to reduce one atomic unit of vanadium, that is,  
30  $\text{V}^{+5}\text{V}^{+5}$  to  $\text{V}^{+5}\text{V}^{+4}$ . The predominate reaction is C to  $\text{CO}_2$  where for each atomic unit of carbon at ground state zero, a plus 4 oxidation state results. Correspondingly, for each  $1/4$  atomic unit of carbon, one atomic unit of

vanadium is reduced from  $V^{+5}$  to  $V^{+4}$ . (See Reaction 5). . .  
The new product, gamma- $LiV_2O_5$ , is air-stable and suitable  
as an electrode material for an ion cell or rocking chair  
battery.

5           The convenience and energy efficiency of the  
present process can also be contrasted to known methods  
for forming products under reducing atmosphere such as  $H_2$   
which is difficult to control, and from complex and  
expensive precursors. In the present invention, carbon  
10 is the reducing agent, and simple, inexpensive and even  
naturally occurring precursors are useable. For example,  
it is possible to produce  $LiFePO_4$  from  $Fe_2O_3$ , a simple  
common oxide. (See Reaction 1b). The production of  
 $LiFePO_4$  provides a good example of the thermodynamic and  
15 kinetic features of the method. Iron phosphate is  
reduced by carbon and lithiated over a broad temperature  
range. At about  $600^\circ C$ , the C to  $CO_2$  reaction  
predominates and takes about a week to complete. At  
about  $750^\circ C$ , the C to CO reaction predominates and takes  
20 about 8 hours to complete. The C to  $CO_2$  reaction  
requires less carbon reductant but takes longer due to  
the low temperature kinetics. The C to CO reaction  
requires about twice as much carbon, but due to the high  
temperature reaction kinetics, it proceeds relatively  
25 fast. In both cases, the Fe in the precursor  $Fe_2O_3$  has  
oxidation state +3 and is reduced to oxidation (valence)  
state +2 in the product  $LiFePO_4$ . The C to CO reaction  
requires that  $\frac{1}{2}$  atomic unit of carbon be used for each  
atomic unit of Fe reduced by one valence state. The CO  
30 to  $CO_2$  reaction requires that  $\frac{1}{4}$  atomic unit of carbon  
be used for each atomic unit of Fe reduced by one valence  
state.

The active materials of the invention are also characterized by being stable in an as-prepared condition, in the presence of air and particularly humid air. This is a striking advantage, because it facilitates preparation of and assembly of battery cathodes and cells, without the requirement for controlled atmosphere. This feature is particularly important, as those skilled in the art will recognize that air stability, that is, lack of degradation on exposure to air, is very important for commercial processing. Air-stability is known in the art to more specifically indicate that a material does not hydrolyze in presence of moist air. Generally, air-stable materials are also characterized by Li being extracted therefrom above about 3.0 volts versus lithium. The higher the extraction potential, the more tightly bound the lithium ions are to the host lattice. This tightly bound property generally confers air stability on the material. The air-stability of the materials of the invention is consistent with the stability demonstrated by cycling at the conditions stated herein. This is in contrast to materials which insert Li at lower voltages, below about 3.0 volts versus lithium, and which are not air-stable, and which hydrolyze in moist air.

While this invention has been described in terms of certain embodiments thereof, it is not intended that it be limited to the above description, but rather only to the extent set forth in the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined in the following claims.



What Is Claimed Is:

1. A method of making a lithium mixed metal compound by reaction of starting materials which comprises: mixing starting materials in particle form, said starting materials comprising a metal compound, a lithium compound having a melting point greater than 450°C, and carbon, where said carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and heating said starting materials in a non-oxidizing atmosphere at a temperature sufficient to form a reaction product comprising lithium and said reduced metal ion.

2. The method of claim 1 wherein said lithium compound is selected from the group consisting of lithium carbonate, lithium phosphate, lithium oxide, lithium vanadate, and mixtures thereof.

3. The method of claim 1 wherein said metal compound is a compound of a metal selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr, and mixtures thereof.

4. The method of claim 3 wherein said metal compound is selected from the group consisting of  $\text{Fe}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{FePO}_4$ ,  $\text{VO}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{LiVO}_3$ ,  $\text{NH}_4\text{VO}_3$ , and mixtures thereof.

5. The method of claim 1 wherein said starting materials include a second metal compound having a second

metal ion which is not reduced and which forms a part of said reaction product.

6. The method of claim 1 wherein said starting materials include a second metal compound which is a compound of a metal selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof.

7. The method of claim 6 wherein said second metal compound is selected from the group consisting of magnesium hydroxide and calcium hydroxide.

8. The method of claim 1 wherein said starting materials include a phosphate compound and said reaction product is a lithium metal phosphate.

9. The method of claim 8 wherein said phosphate compound is selected from the group consisting of diammonium hydrogen phosphate, ammonium dihydrogen phosphate, lithium dihydrogen phosphate, and mixtures thereof.

10. The method of claim 1 wherein said metal compound is a metal oxide or a metal phosphate.

11. The method of claim 1 wherein said metal compound is  $V_2O_5$ , and said lithium compound is lithium carbonate.

12. The method of claim 1 wherein said mixing and heating are conducted in a first stage by mixing starting materials consisting of iron oxide, diammonium hydrogen phosphate and carbon and heating said first stage mixed starting materials at a temperature

sufficient to produce iron phosphate; and in a second stage by mixing starting materials consisting of said iron phosphate and lithium phosphate and heating said second stage mixed starting materials at a temperature sufficient to form lithium iron phosphate represented by the nominal formula  $\text{LiFePO}_4$ .

13. A method of making a lithium mixed metal compound by reaction of starting materials which comprises:

mixing starting materials in particle form, said starting materials comprising a metal compound; a lithium compound; carbon present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and a compound containing a polyanion capable of forming a crystal lattice; and

heating said starting materials in a non-oxidizing atmosphere at a temperature sufficient to form a single phase reaction product comprising lithium, said reduced metal ion, and said polyanion.

14. The method of claim 13 wherein said lithium compound is lithium carbonate, said metal compound is a metal oxide, and said polyanion-containing compound is a phosphate compound.

15. The method of claim 13 wherein said starting materials consist of: iron oxide; a hydroxide selected from the group consisting of magnesium hydroxide and calcium hydroxide; lithium carbonate; a phosphate selected from the group consisting of diammonium hydrogen phosphate and ammonium dihydrogen phosphate; and carbon.

16. The method of claim 13 wherein said starting materials consist of: lithium carbonate; iron phosphate; diammonium hydrogen phosphate; a hydroxide selected from the group consisting of magnesium hydroxide and calcium hydroxide; and carbon.

17. The method of claim 13 wherein said starting materials comprise: two of said metal compounds, the first being an oxide of a transition metal selected from Groups 4 to 11 inclusive of the Periodic Table having a +2 valence state, and the second being a compound of a metal selected from Groups 2, 12, and 14 of the Periodic Table having a +2 valence state; said lithium compound selected from the group consisting of lithium carbonate and lithium dihydrogen phosphate; and said polyanion containing compound selected from the group consisting of diammonium hydrogen phosphate, ammonium dihydrogen phosphate, lithium dihydrogen phosphate, and mixtures thereof.

18. The method of claim 13 wherein said starting materials consist of lithium carbonate, iron oxide and a phosphate of a metal selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof.

19. A method of making a single phase compound which comprises: mixing starting materials in particle form, said starting materials comprising a metal compound, a lithium compound selected from the group consisting of lithium acetate ( $\text{LiOOCCH}_3$ ), lithium nitrate ( $\text{LiNO}_3$ ), lithium oxalate ( $\text{Li}_2\text{C}_2\text{O}_4$ ), lithium oxide ( $\text{Li}_2\text{O}$ ), lithium phosphate ( $\text{Li}_3\text{PO}_4$ ), lithium dihydrogen phosphate ( $\text{LiH}_2\text{PO}_4$ ), lithium vanadate ( $\text{LiVO}_3$ ), and lithium carbonate

( $\text{Li}_2\text{CO}_2$ ), and carbon present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and heating said starting materials in a non-oxidizing atmosphere at a temperature sufficient to form a single phase reaction product.

20. The method of claim 19 wherein said metal compound is a compound of a metal selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr, and mixtures thereof.

21. The method of claim 20 wherein said metal compound is selected from the group consisting of  $\text{Fe}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{FePO}_4$ ,  $\text{VO}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{LiVO}_3$ ,  $\text{NH}_4\text{VO}_3$ , and mixtures thereof.

22. The method of claim 19 wherein said starting materials include a second metal compound having a second metal ion which is not reduced and which forms a part of said reaction product.

23. The method of claim 19 wherein said starting materials include a second metal compound which is a compound of a metal selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof.

24. The method of claim 23 wherein said second metal compound is selected from the group consisting of magnesium hydroxide and calcium hydroxide.

25. The method of claim 19 wherein said

from the group consisting of diammonium hydrogen phosphate, ammonium dihydrogen phosphate, and mixtures thereof.

26. The method of claim 19 wherein said metal compound is a metal oxide or a metal phosphate.

27. The method of claim 19 wherein said metal compound is  $V_2O_5$ , and said lithium compound is lithium carbonate.

28. The method of claim 19 wherein said mixing and heating are conducted in a first stage by mixing starting materials consisting of iron oxide, diammonium hydrogen phosphate and carbon and heating said first stage mixed starting materials at a temperature sufficient to produce iron phosphate; and in a second stage by mixing starting materials consisting of said iron phosphate and lithium phosphate and heating said second stage mixed starting materials at a temperature sufficient to form lithium iron phosphate represented by the nominal formula  $LiFePO_4$ .

29. The method of claim 19 wherein said heating is conducted at a ramp rate of up to about  $10^\circ\text{C}$  per minute to an elevated temperature of between about  $400^\circ\text{C}$  and about  $1200^\circ\text{C}$ , and then maintaining said elevated temperature until said reaction product is formed.

30. The method of claim 29 wherein said elevated temperature is maintained for between several minutes to several hours.

WO 01/53198

1/23

PCT/US00/35438

# 2S1036A1 (LiFePO<sub>4</sub>)

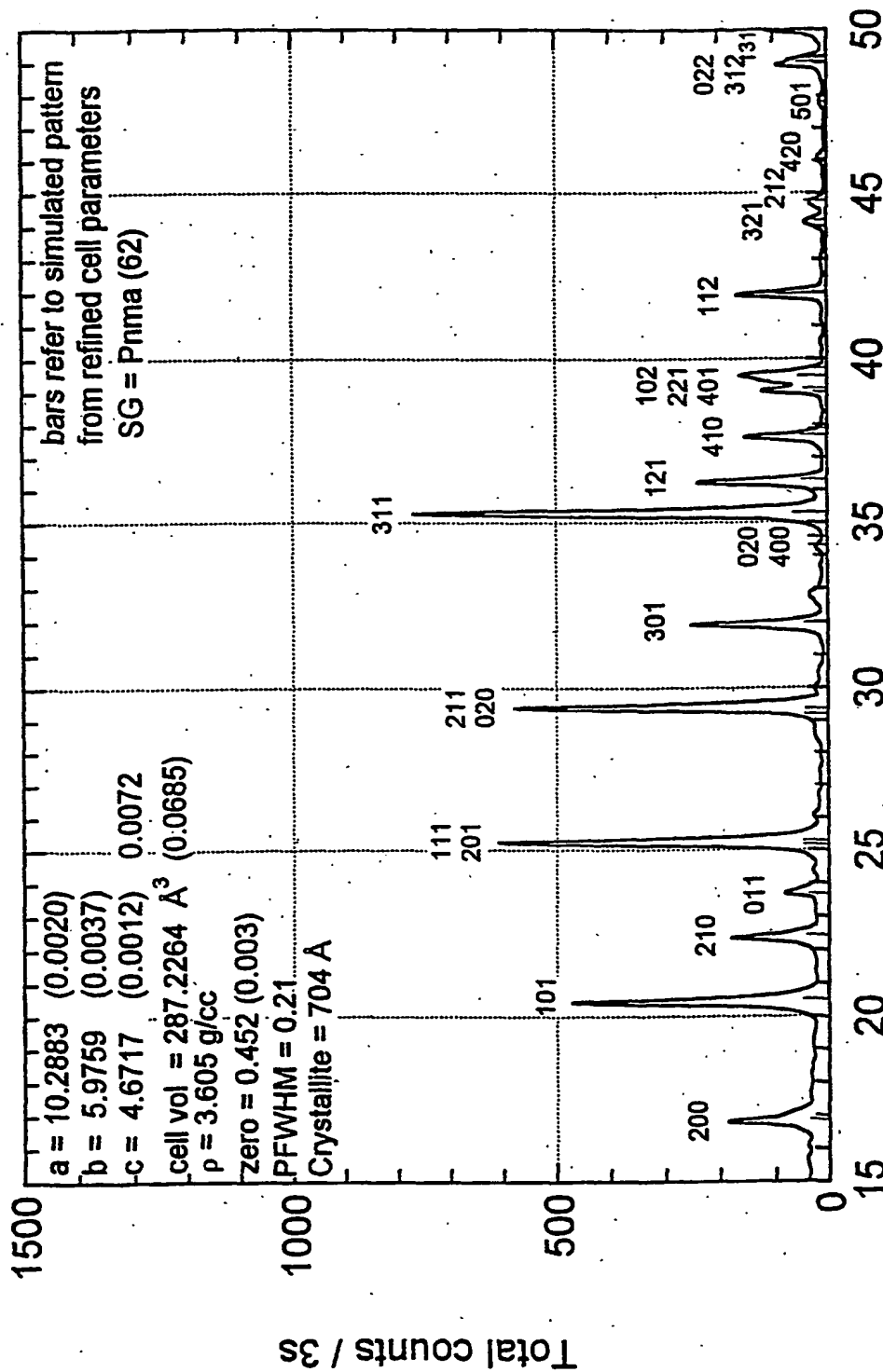


Figure 1

2-Theta / °

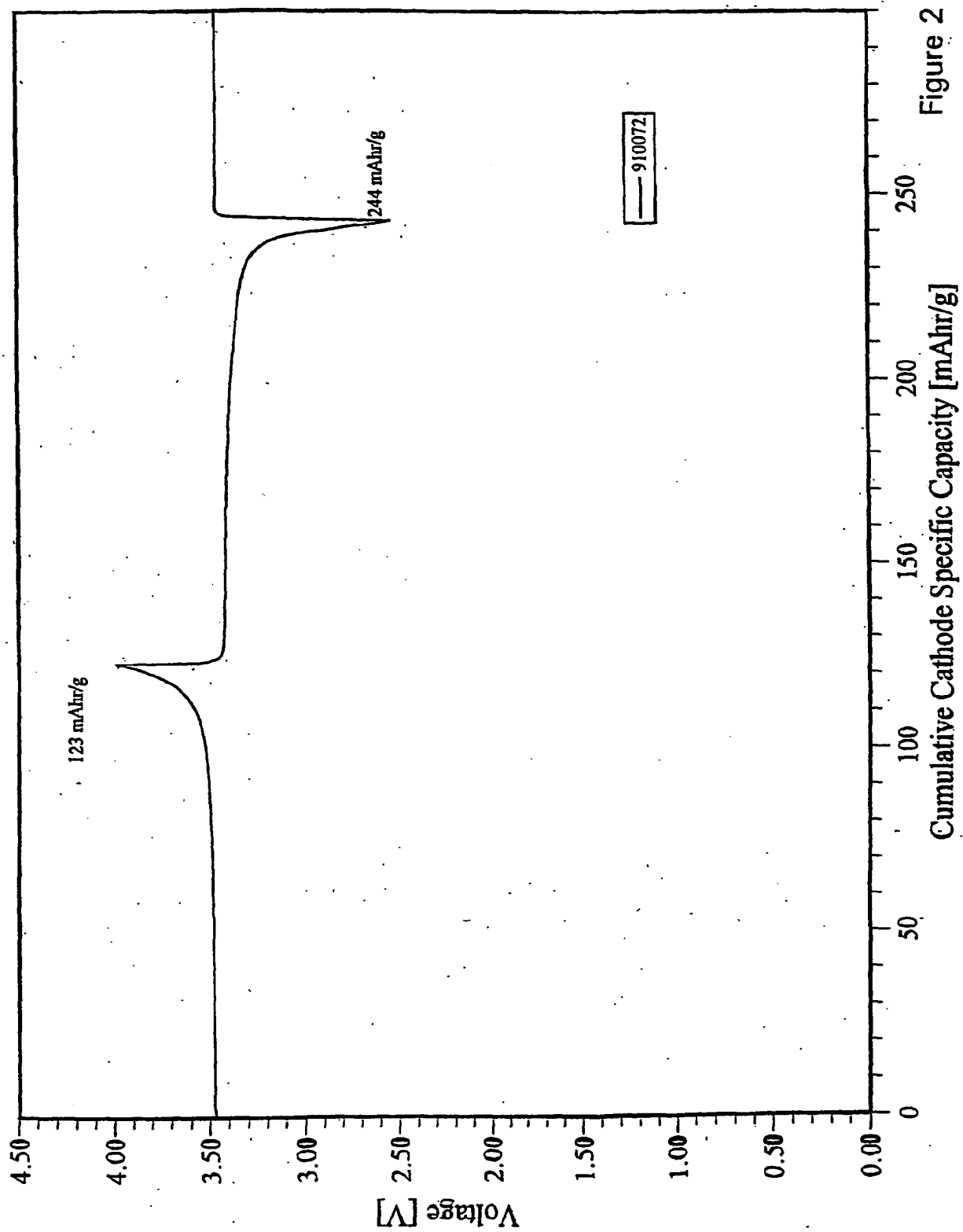
LiFePO<sub>4</sub> 2.5 -4.0 V

Figure 2



WO 01/53198

3/23

PCT/US00/35438

Carbothermal LiFePO<sub>4</sub> vs Li

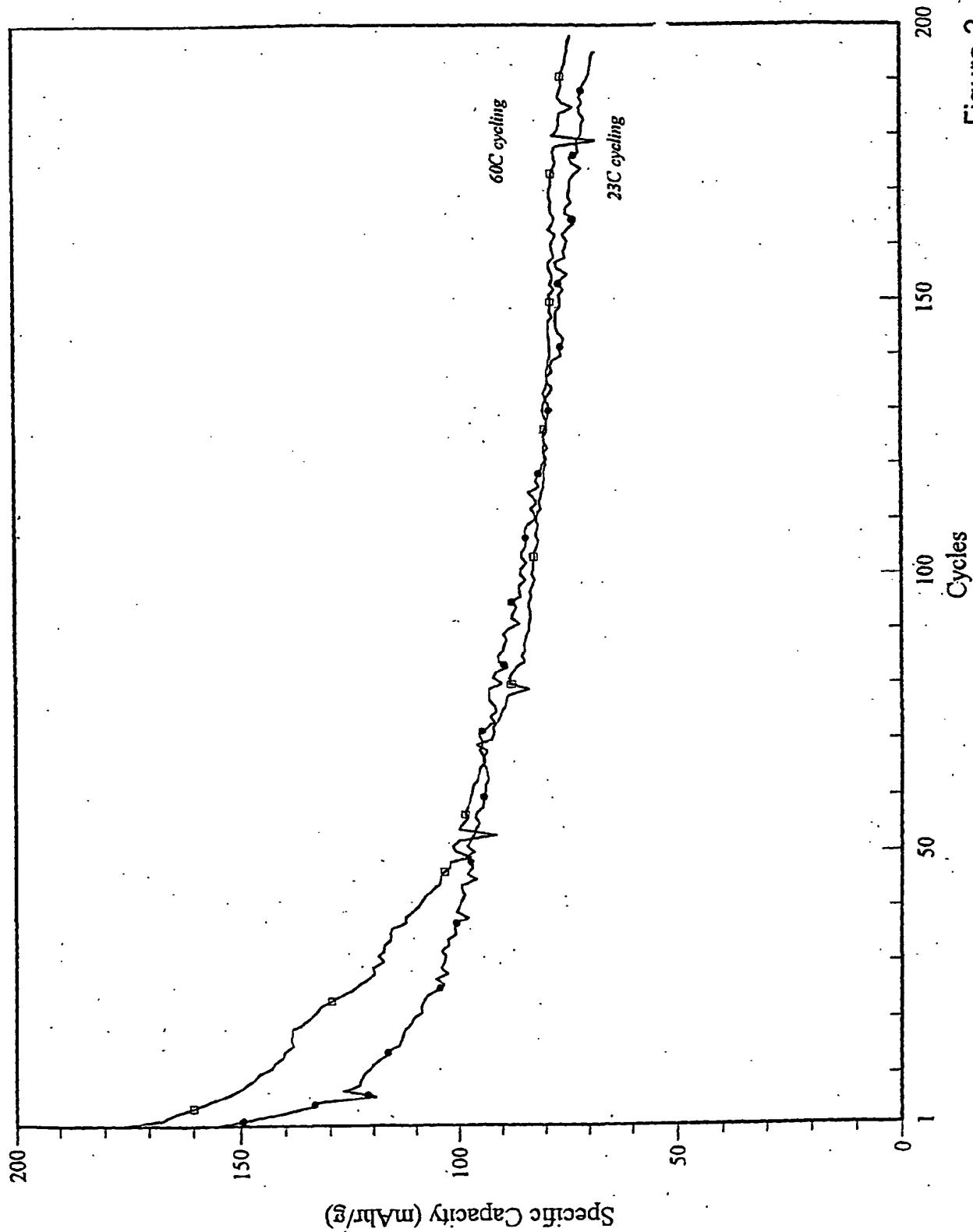


Figure 3

# 1S0937A1 (LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub>)

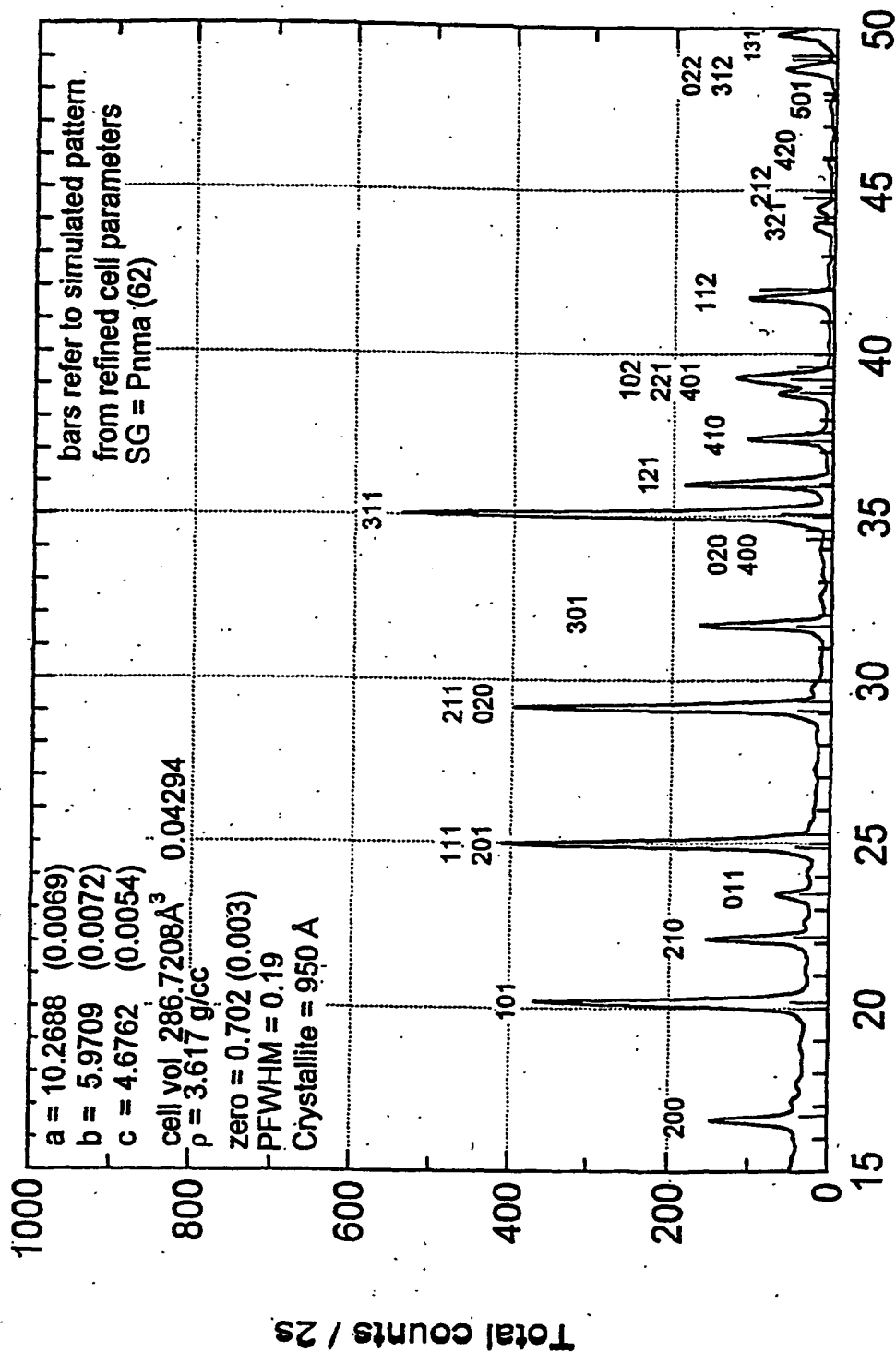


Figure 4

WO 01/53198

5/23

PCT/US00/35438

LiFe<sub>0.9</sub>Mg<sub>0.1</sub>PO<sub>4</sub> 2.5 - 4.0 V

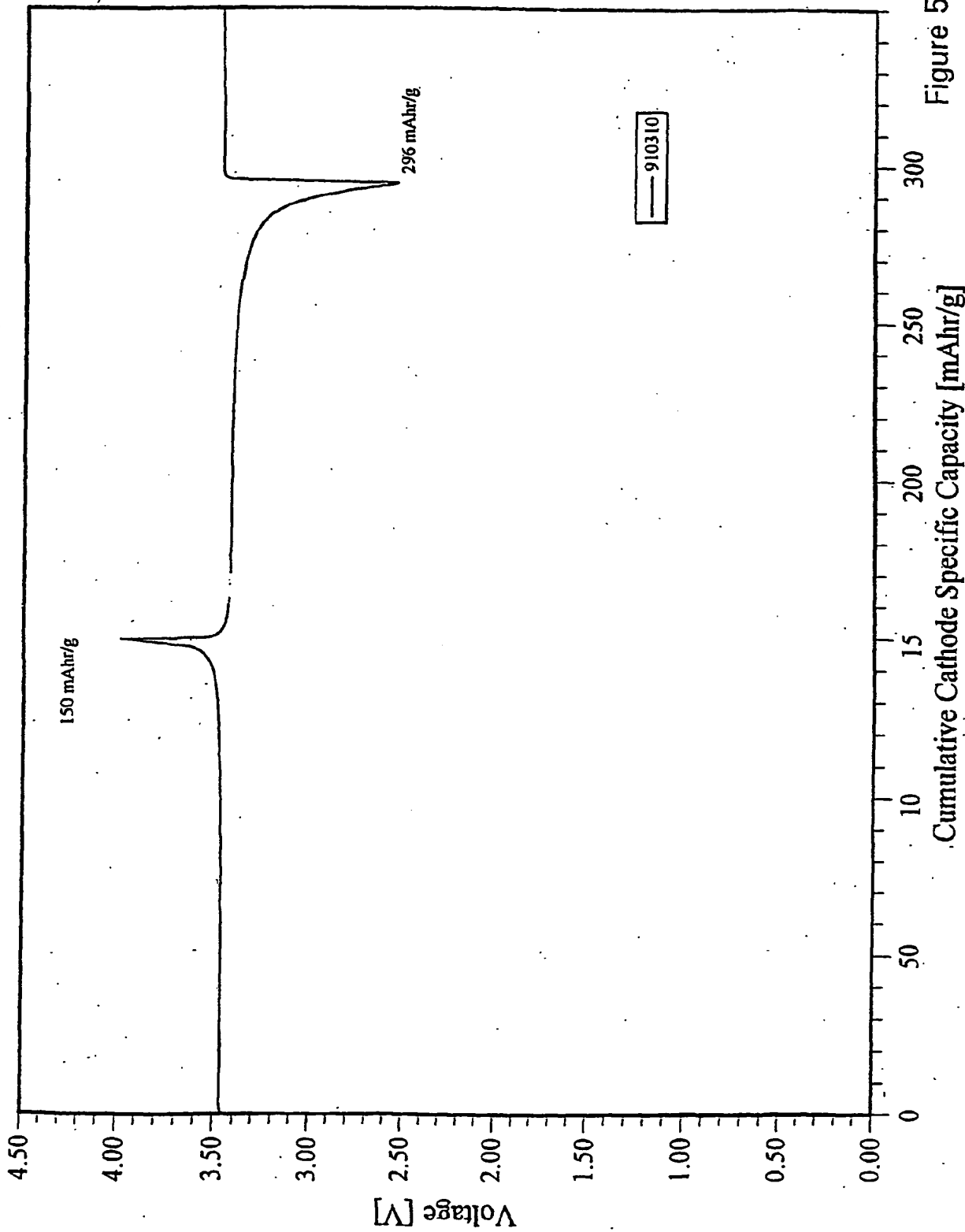


Figure 5

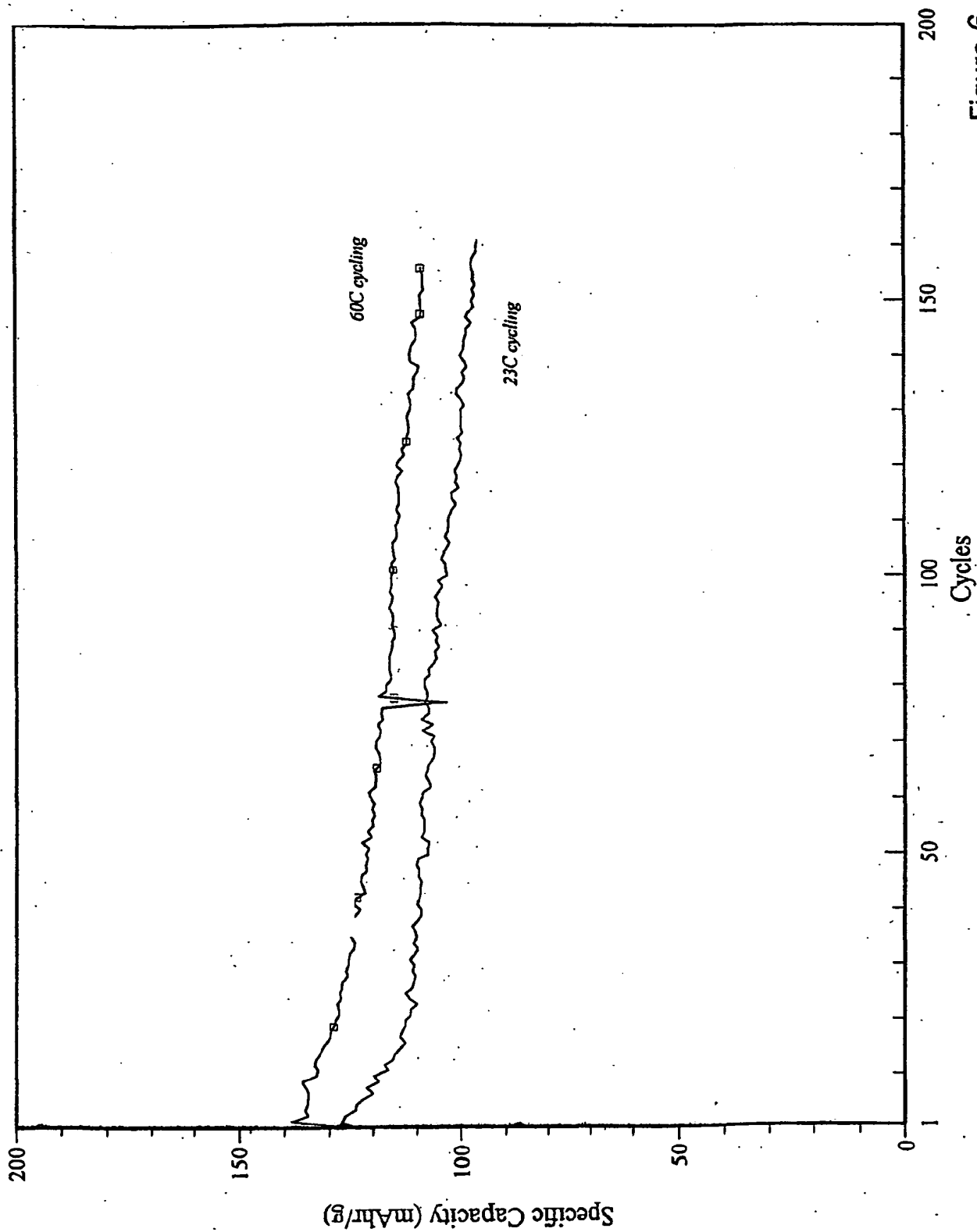
Carbothermal LiMg<sub>0.1</sub>Fe<sub>0.9</sub>PO<sub>4</sub> vs Li

Figure 6

WO 01/53198

7/23

PCT/US00/35438

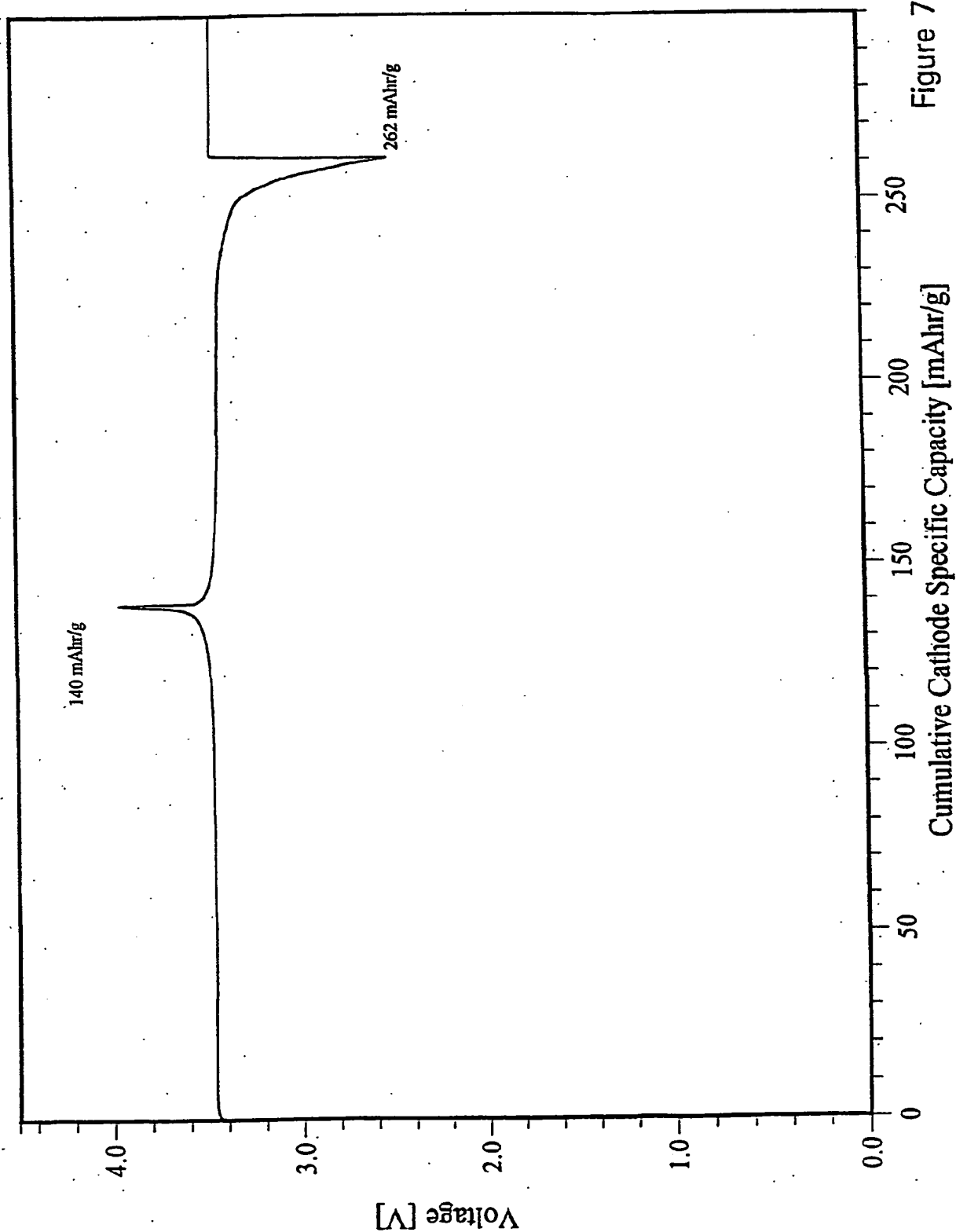
 $\text{LiFe}_0.8\text{Mg}_{0.2}\text{PO}_4$  2.5 - 4.0 V

Figure 7

# 1S0937A1 ( $\text{LiFe}_{0.9}\text{Ca}_{0.1}\text{PO}_4$ )

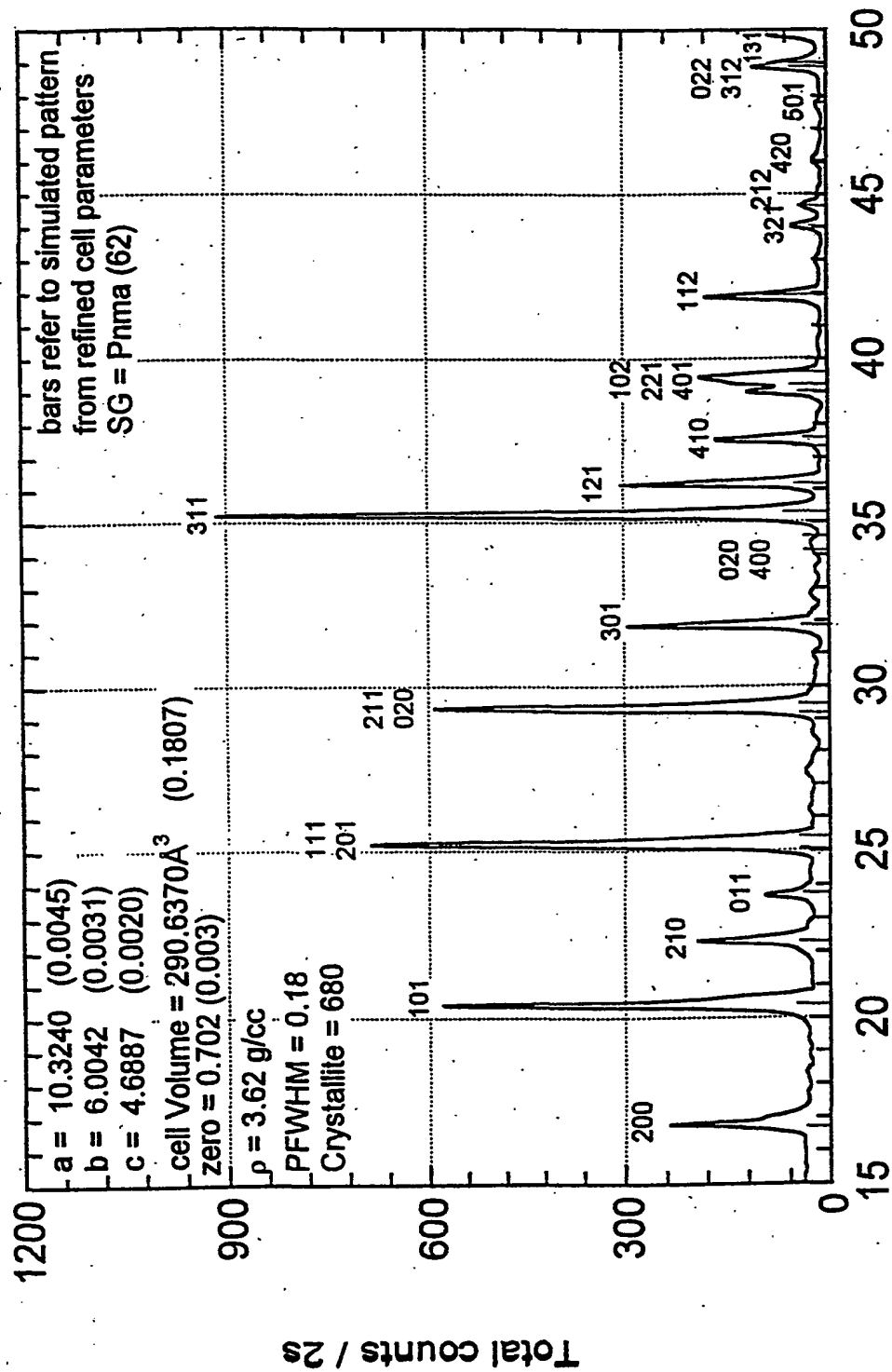


Figure 8

2-Theta / ( $^\circ$ )

WO 01/53198

9/23

PCT/US00/35438

$\text{LiFe}_{0.8}\text{Ca}_{0.2}\text{PO}_4$  2.5 - 4.0 V

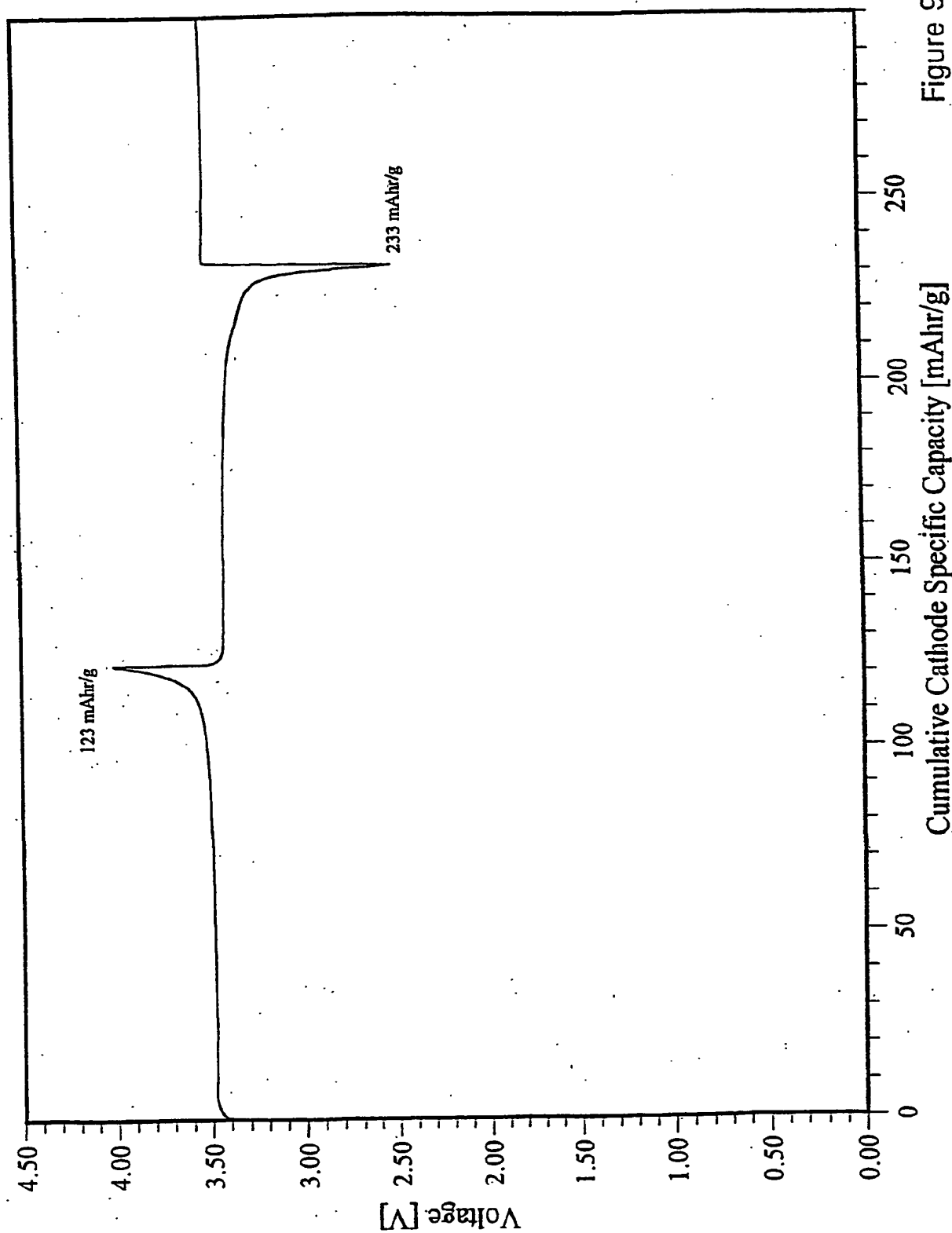


Figure 9

$\text{LiFe}_0.8\text{Zn}_0.2\text{PO}_4$  2.5 - 4.0 V

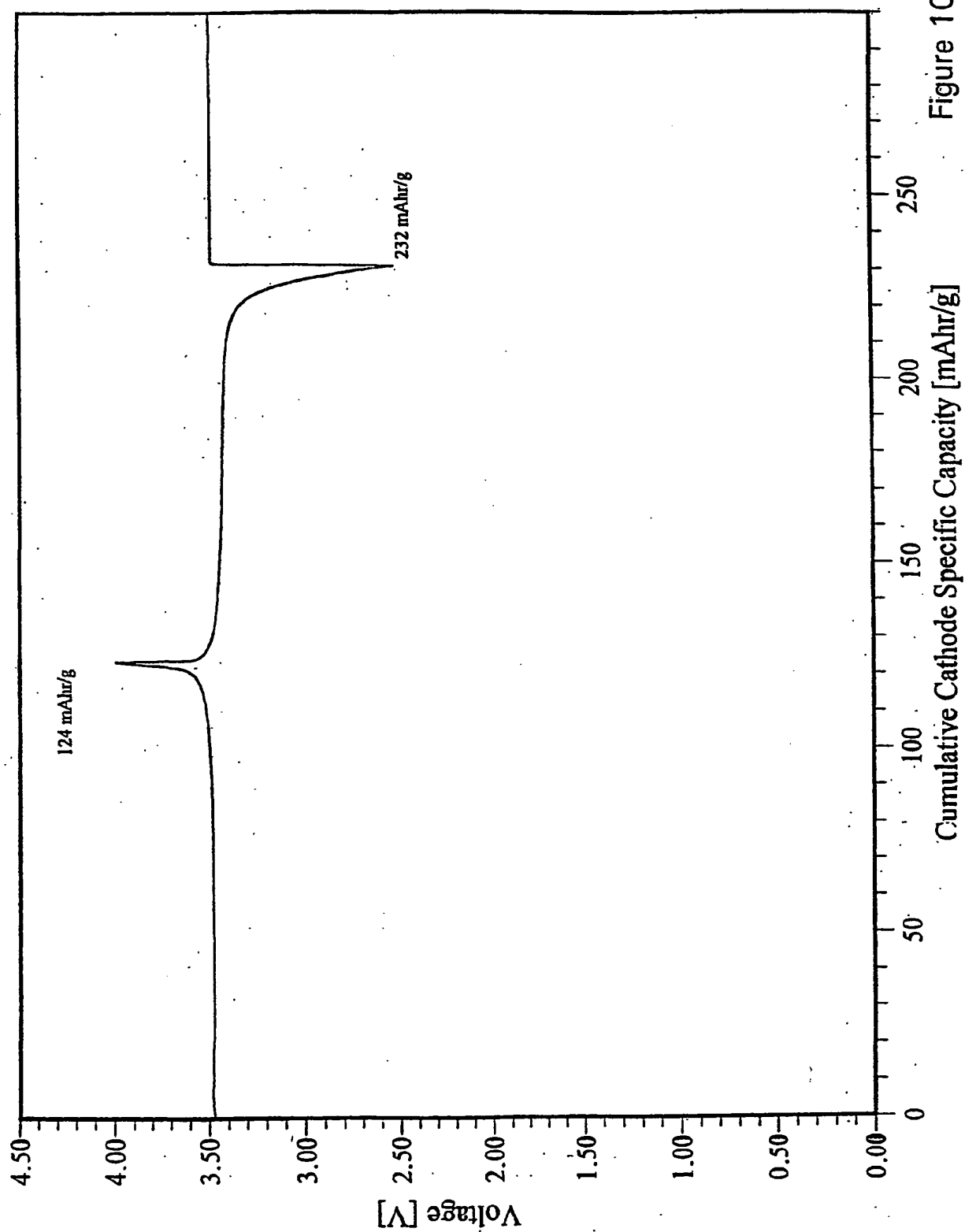


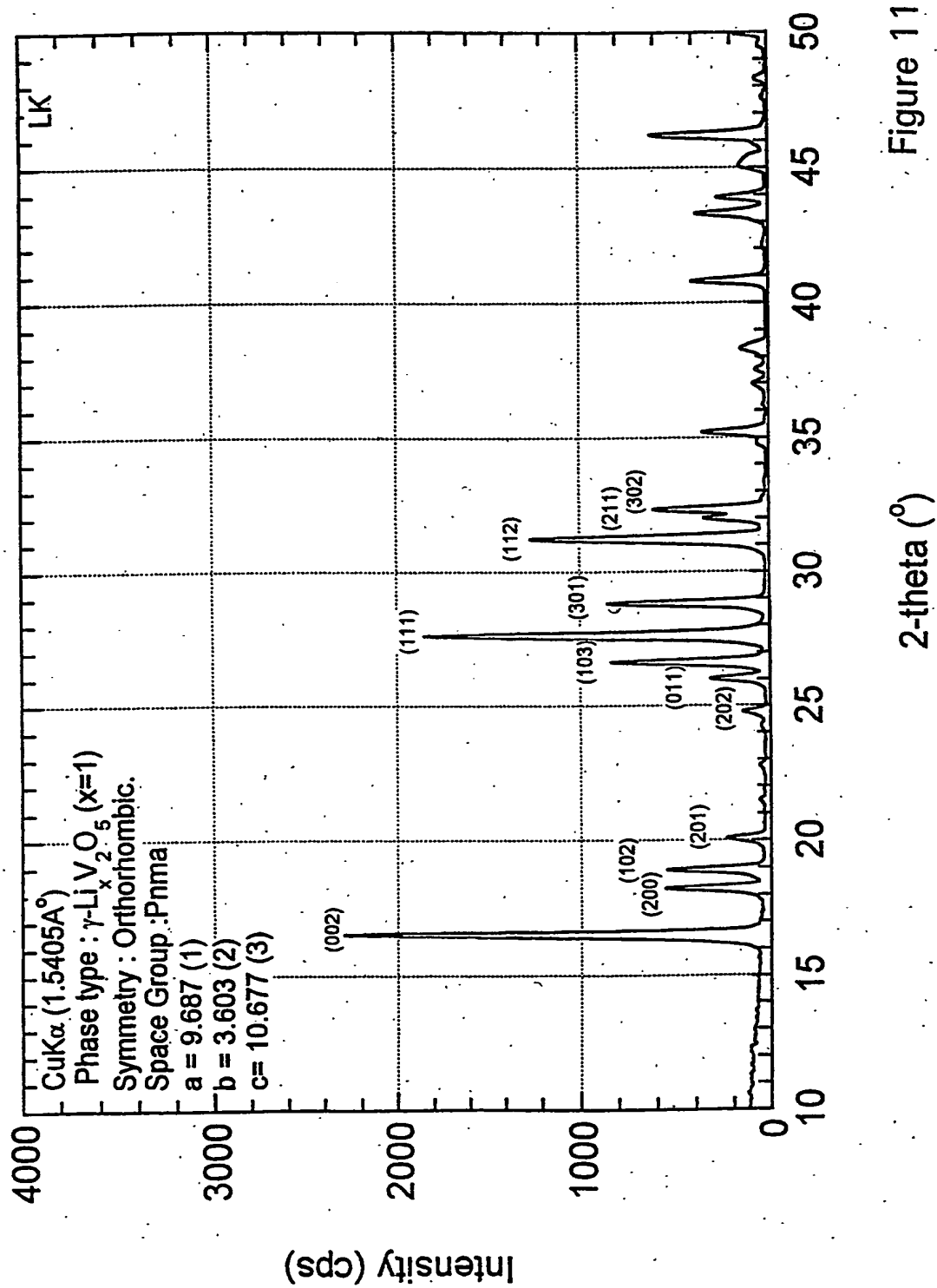
Figure 10



WO 01/53198

11/23

PCT/US00/35438

gamma-  $\text{Li}_x\text{V}_2\text{O}_5$  - carbo-thermal

# $\gamma$ -LiV<sub>2</sub>O<sub>5</sub> Synthesized by Carbothermal Reduction Method

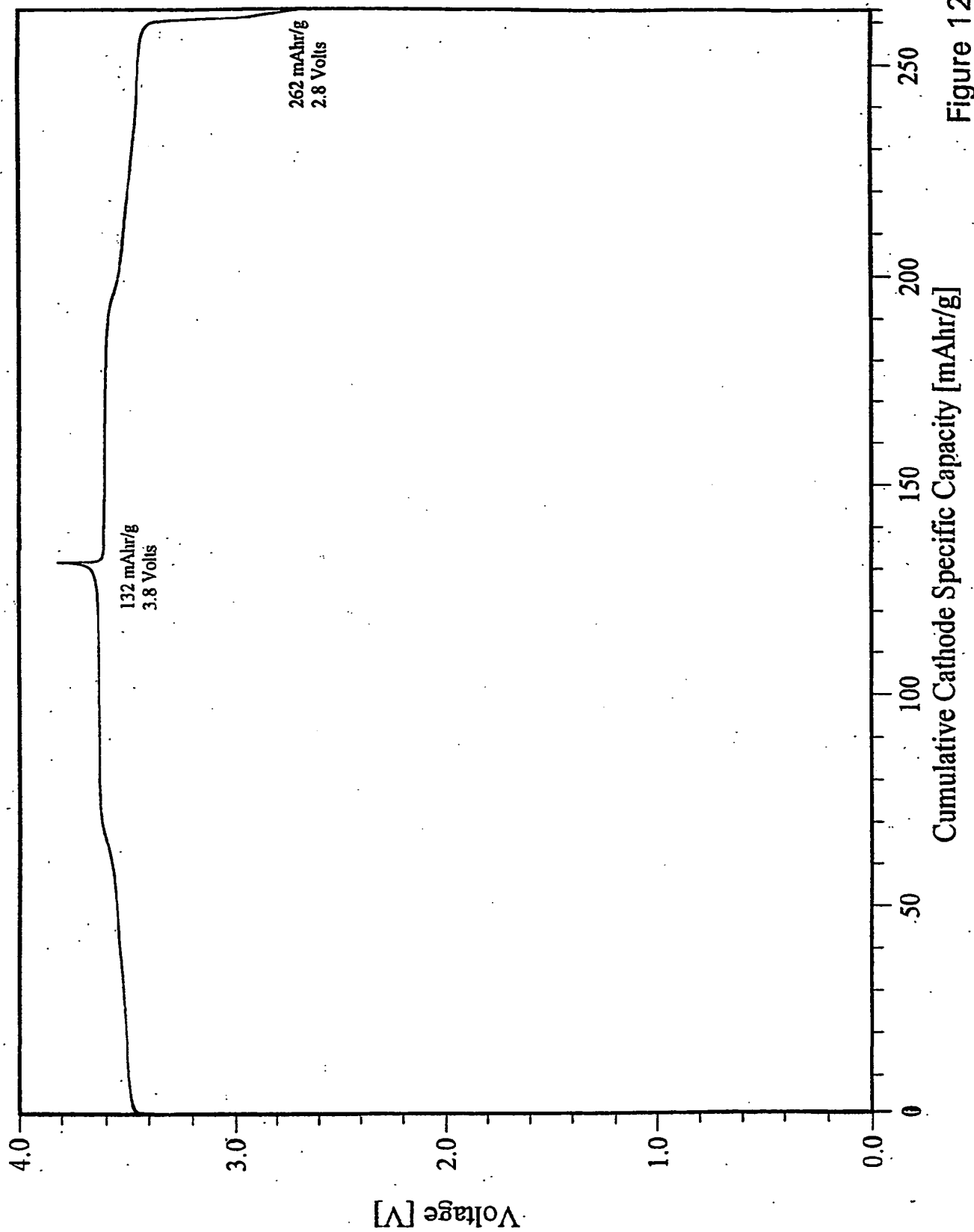


Figure 12

gamma-LiV2O5 vs Li

~C/2 rate, 3.0-3.75V

Carbothermal Reduction Method

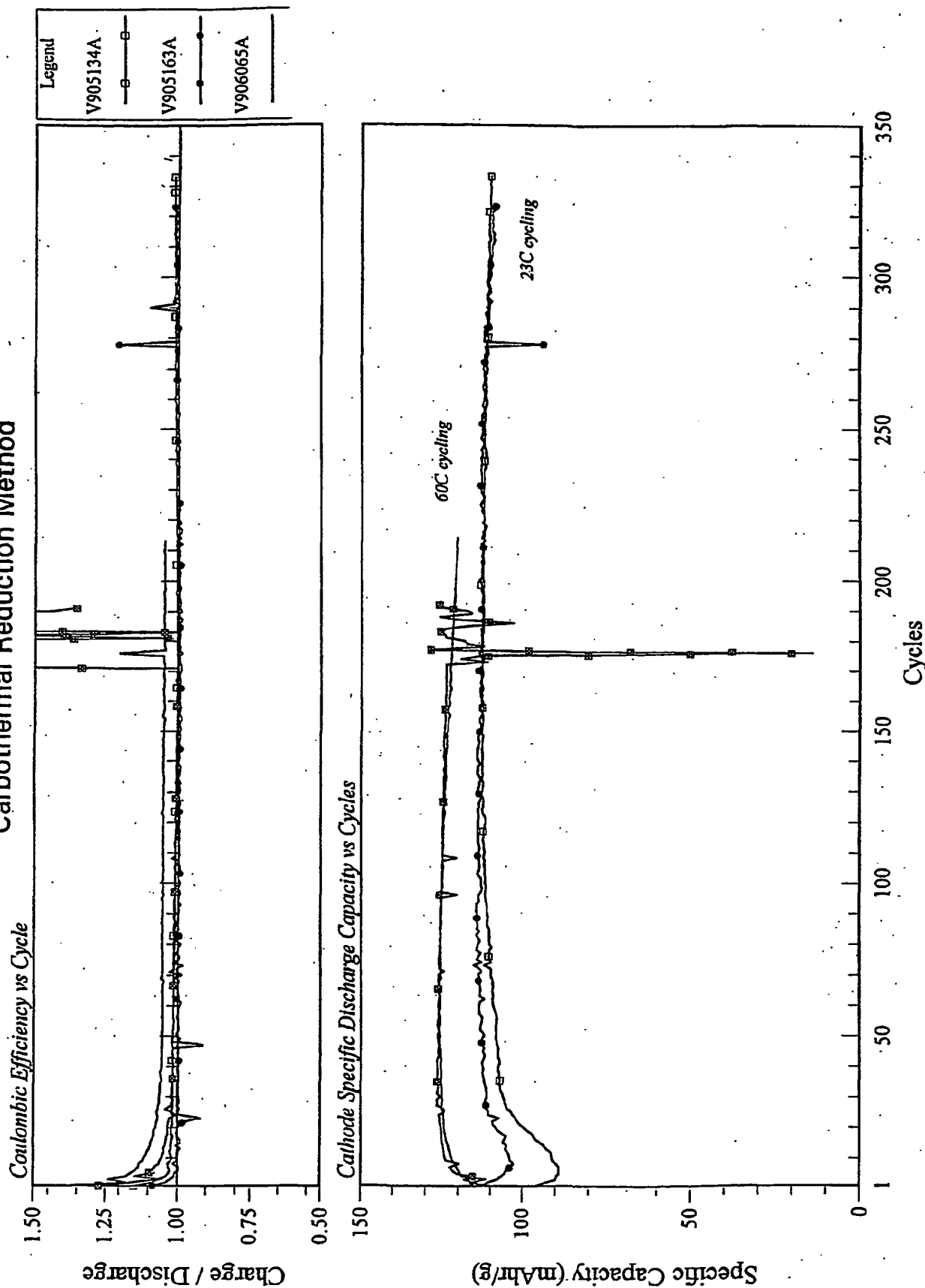


Figure 13

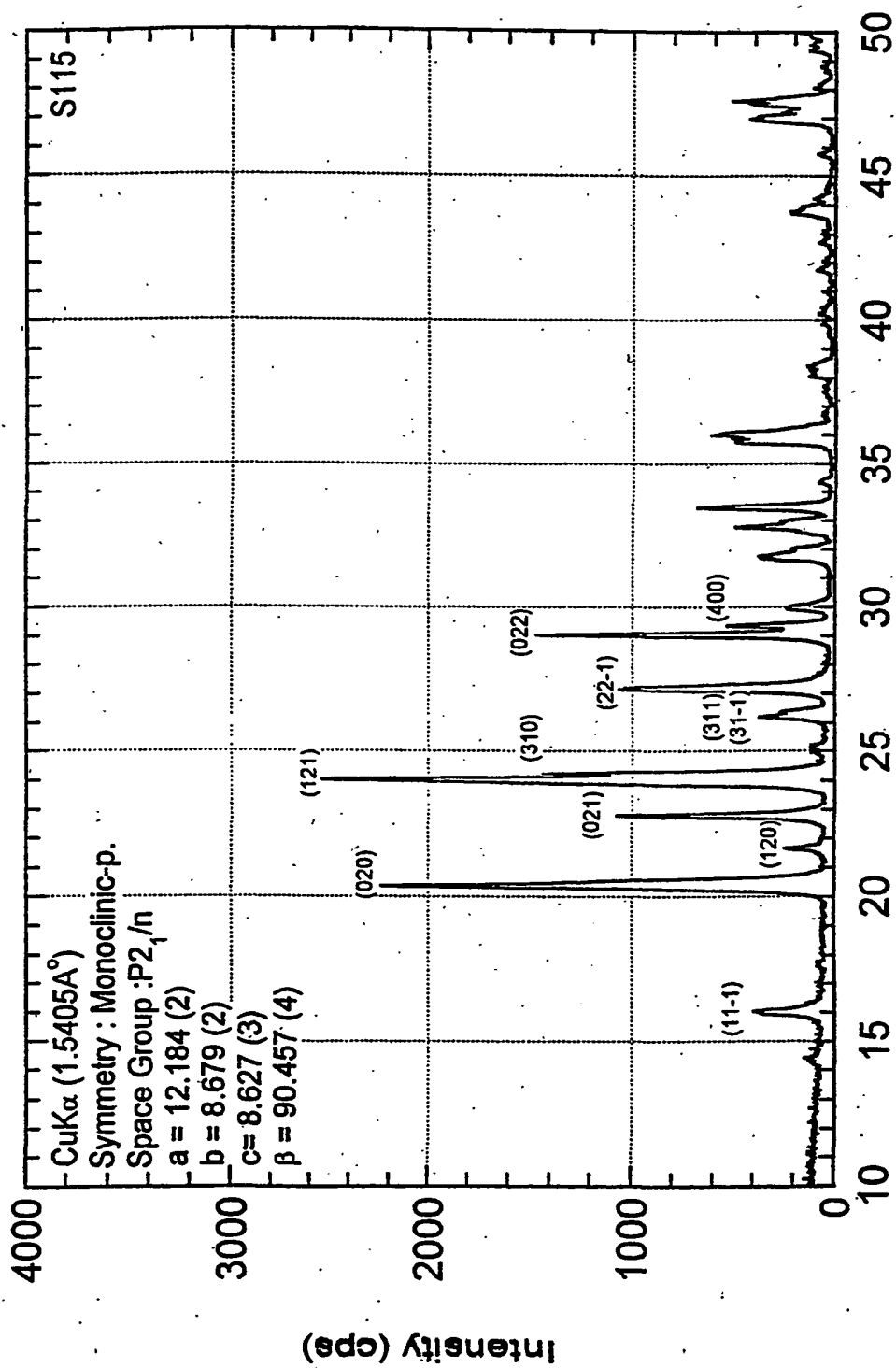
**$\text{Li}_3\text{V}_2(\text{PO}_4)_3$  - carbo-thermal**

Figure 14

2-Theta - ( $^\circ$ )

WO 01/53198

15/23

PCT/US00/35438

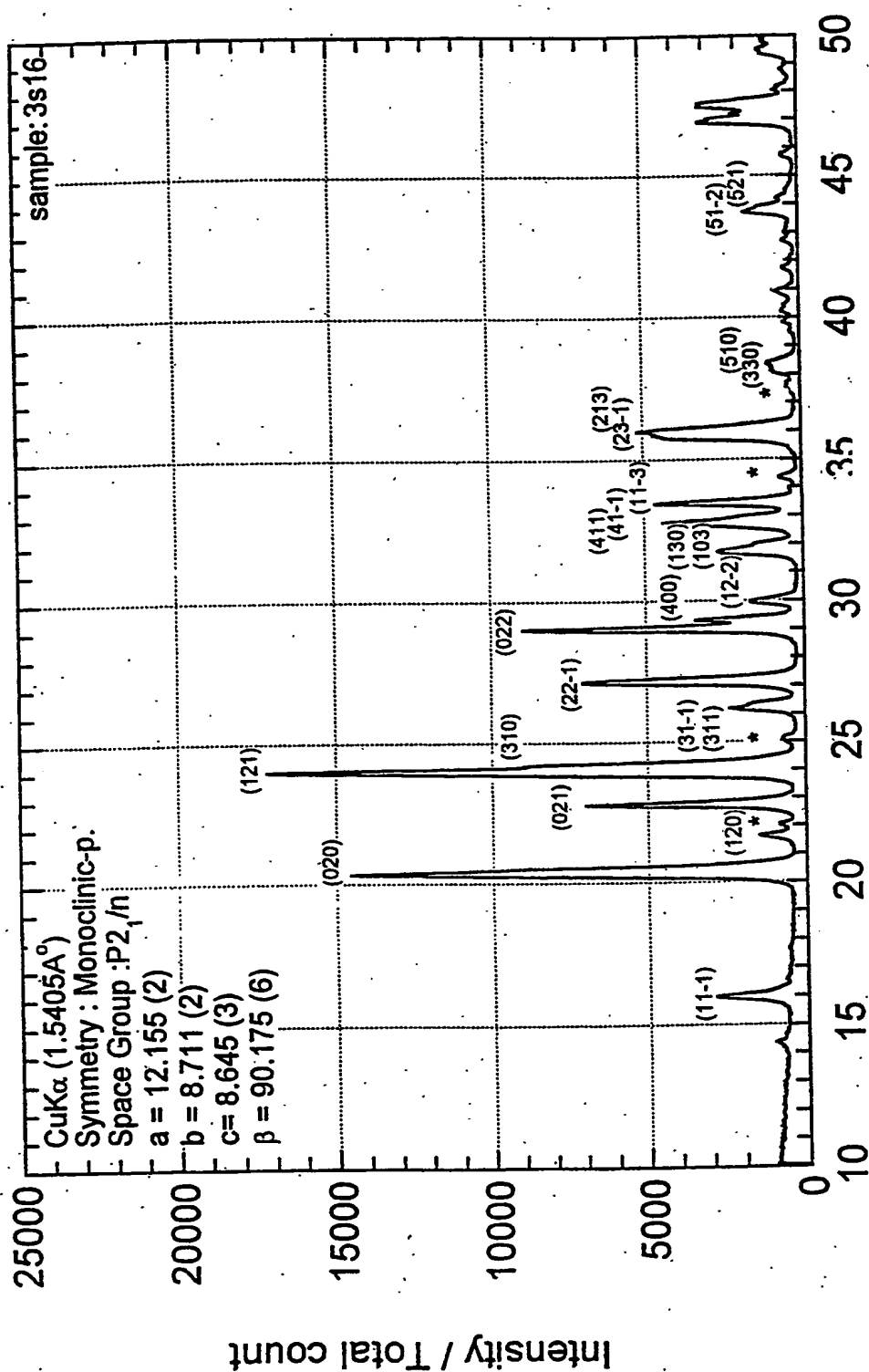


Figure 15

Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> Synthesis by Carbothermal Reduction Method 13.8 mg active

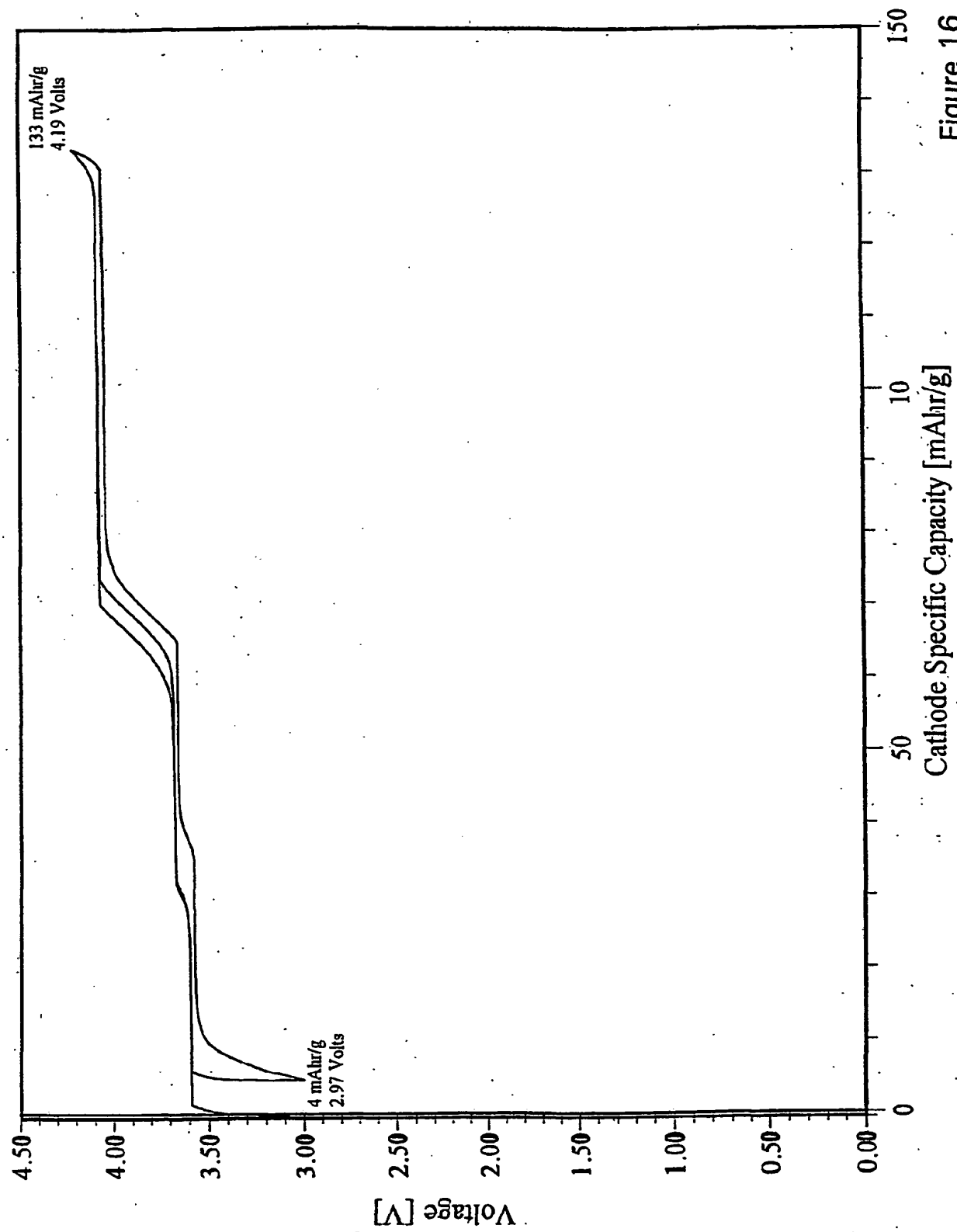


Figure 16

WO 01/53198

17/23

PCT/US00/35438

# $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Synthesis by Carbothermal Reduction Method

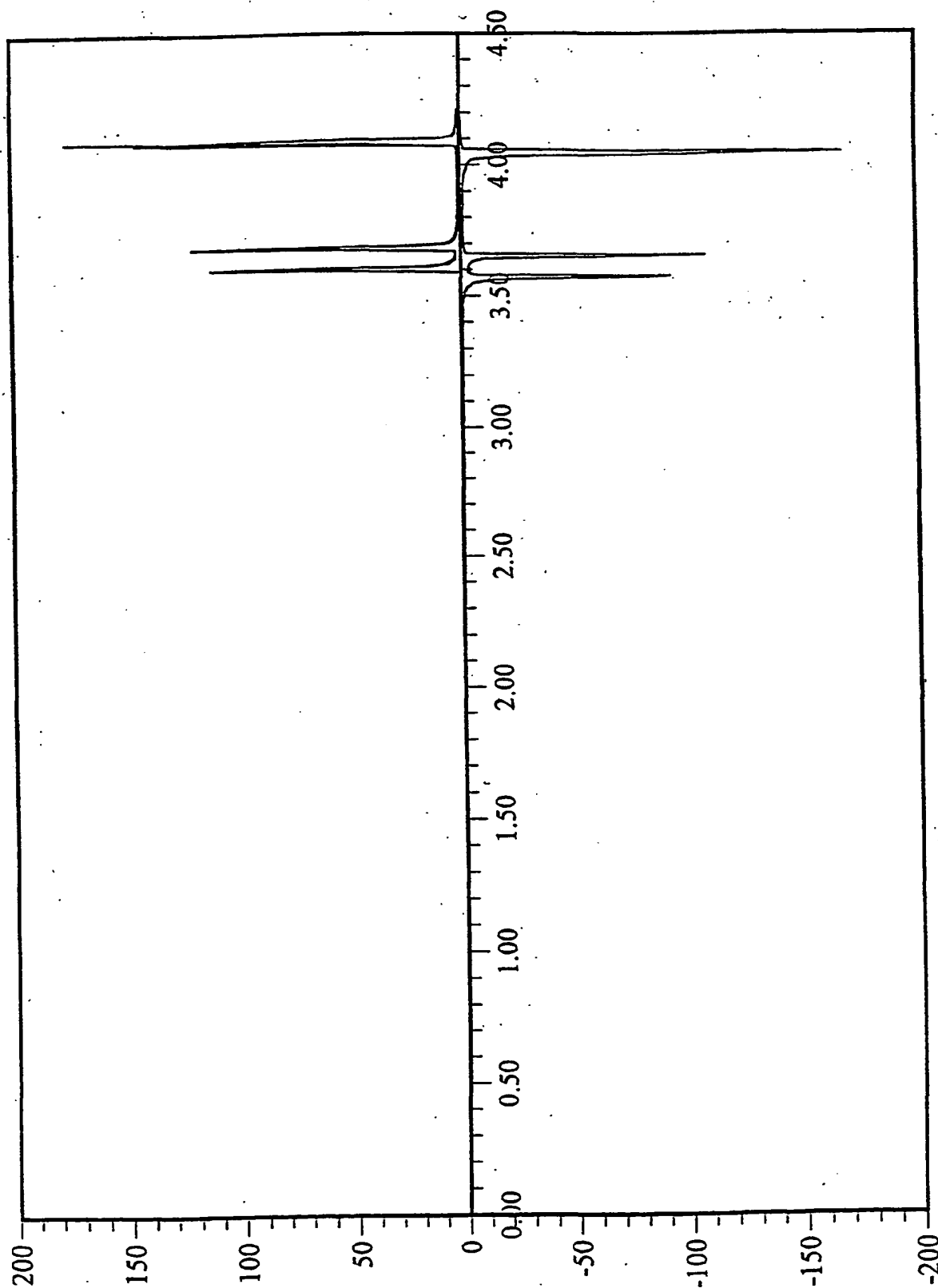


Figure 17

Voltage [V]

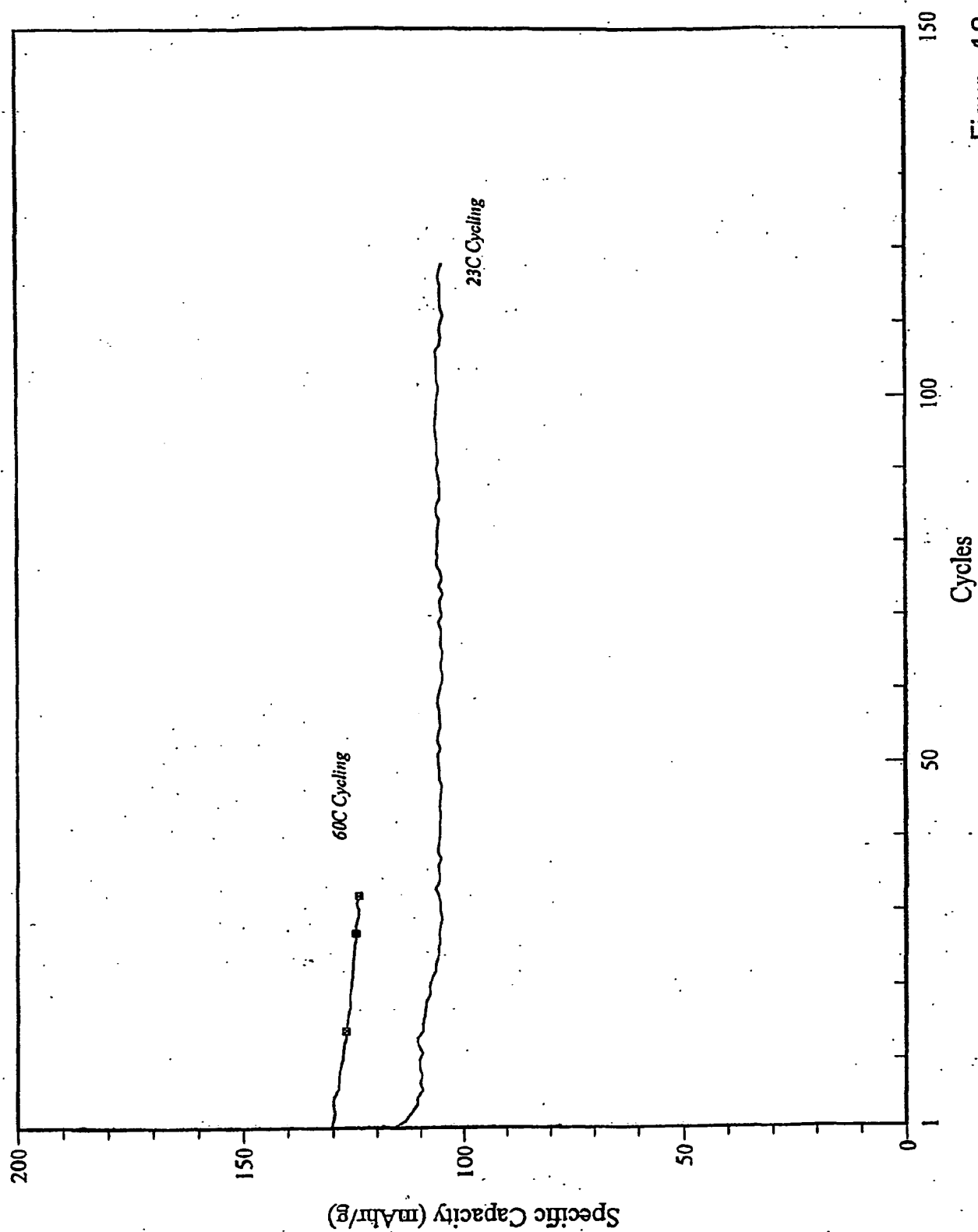
Carbothermal LiMg<sub>0.2</sub>Fe<sub>0.8</sub>PO<sub>4</sub> vs Li

Figure 18



# Voltage Profile for $\text{LiMg}_{0.1}\text{Fe}_{0.9}\text{PO}_4$ vs MCMB

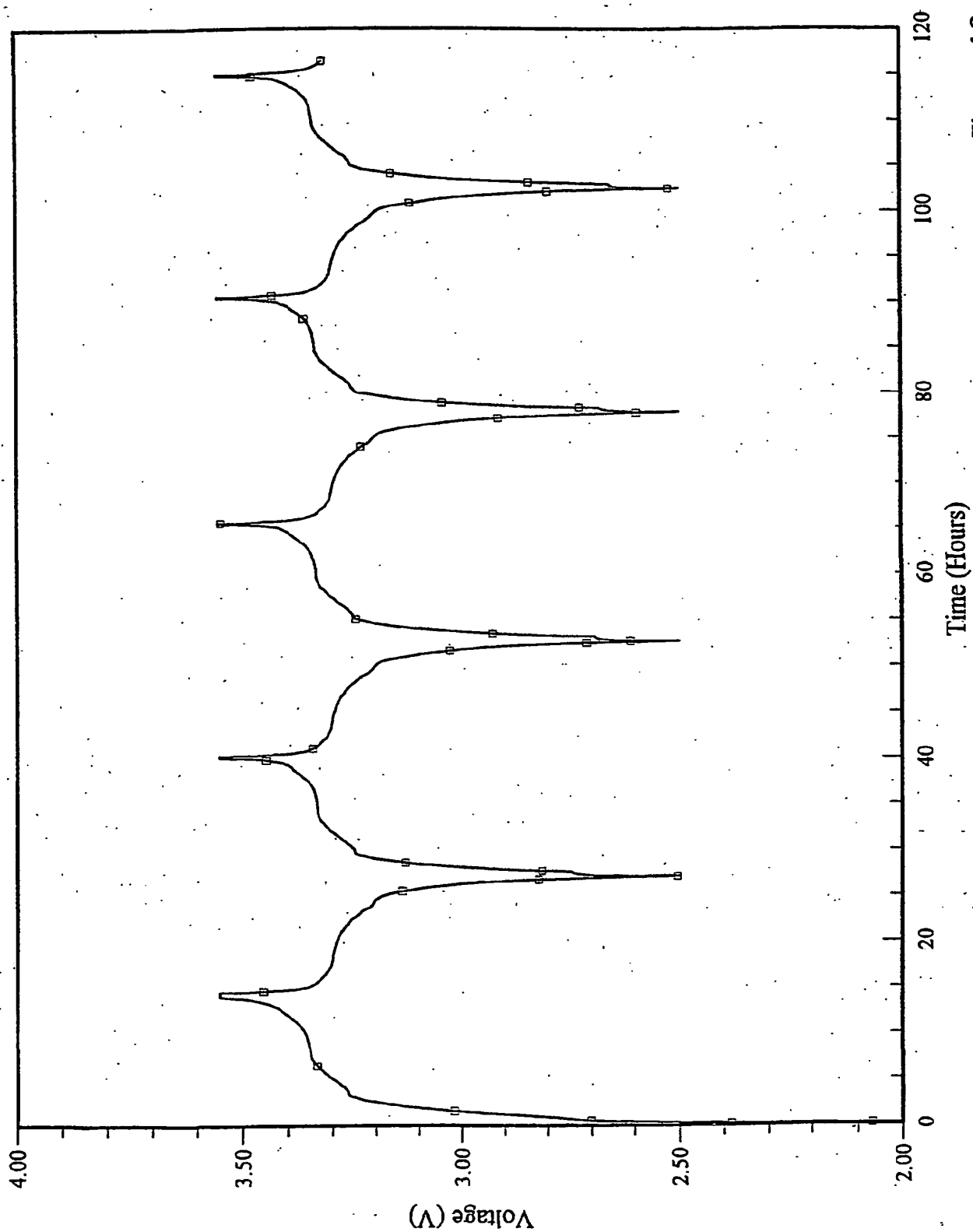


Figure 19

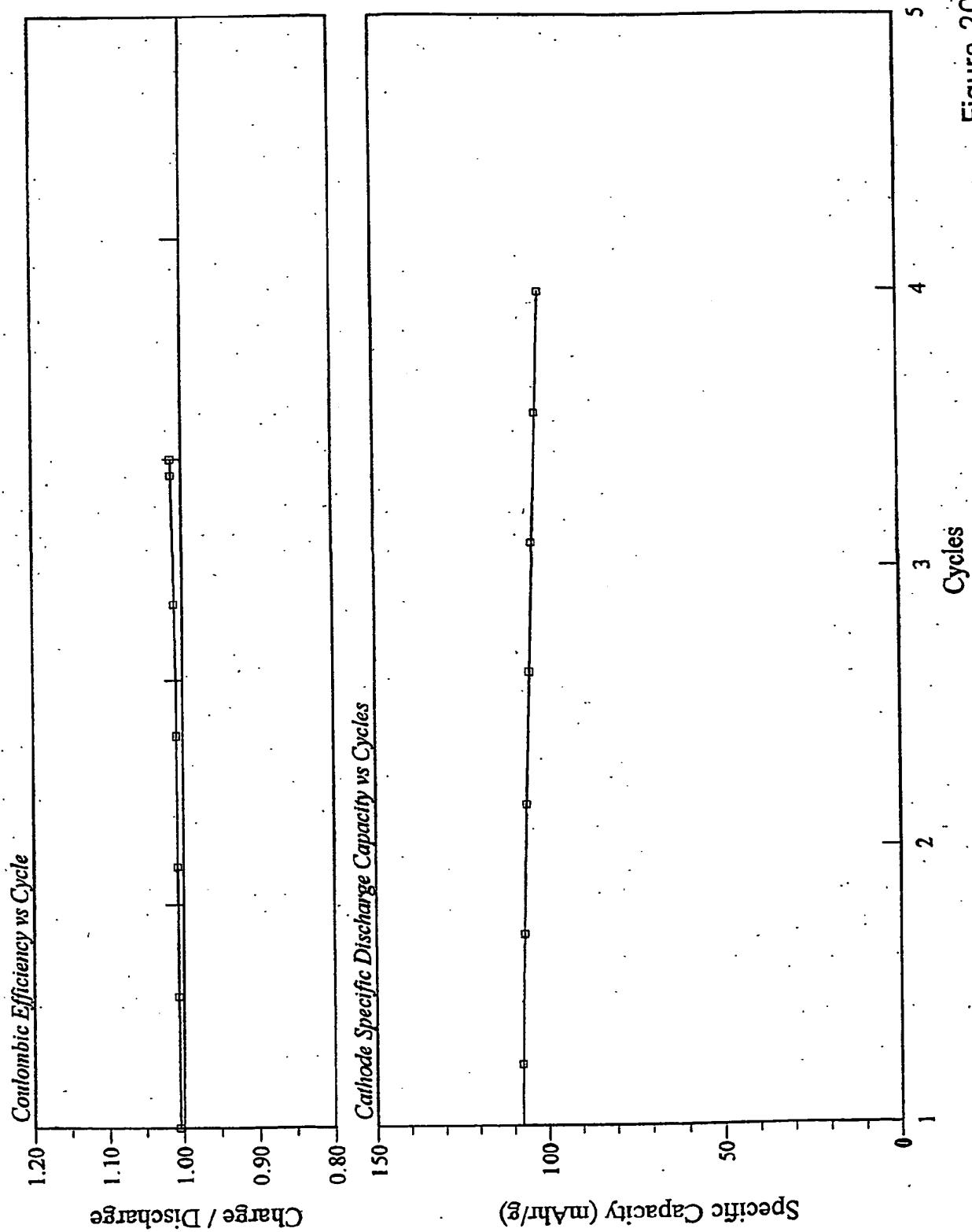
Carbothermal  $\text{LiMg}_{0.1}\text{Fe}_{0.9}\text{PO}_4$  vs MCMB

Figure 20

WO 01/53198

21/23

PCT/US00/35438

Carbothermal  $\text{LiV}_2\text{O}_5/\text{MCMB2528}$  2.5-3.65 V  
gamma- $\text{LiV}_2\text{O}_5$

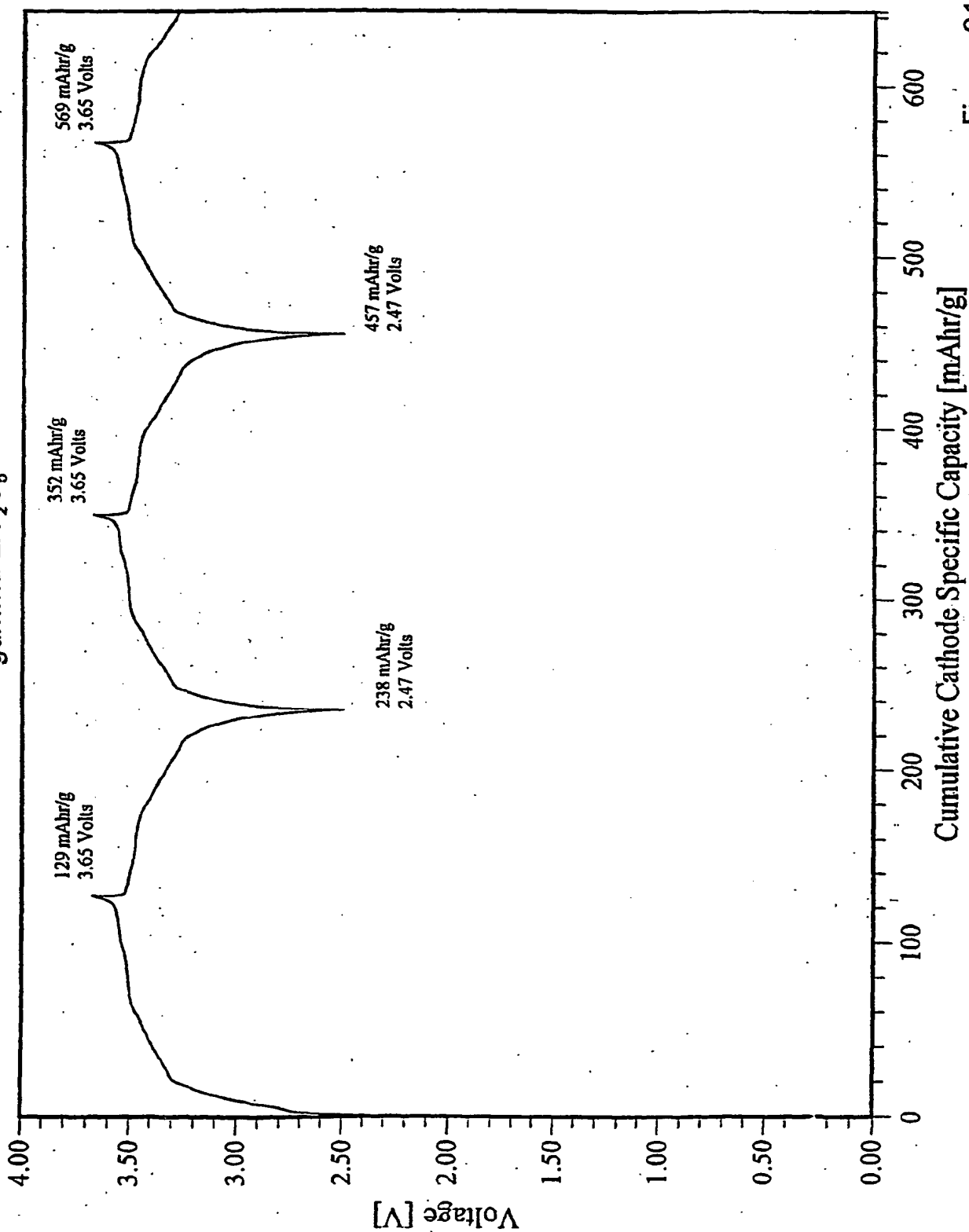


Figure 21

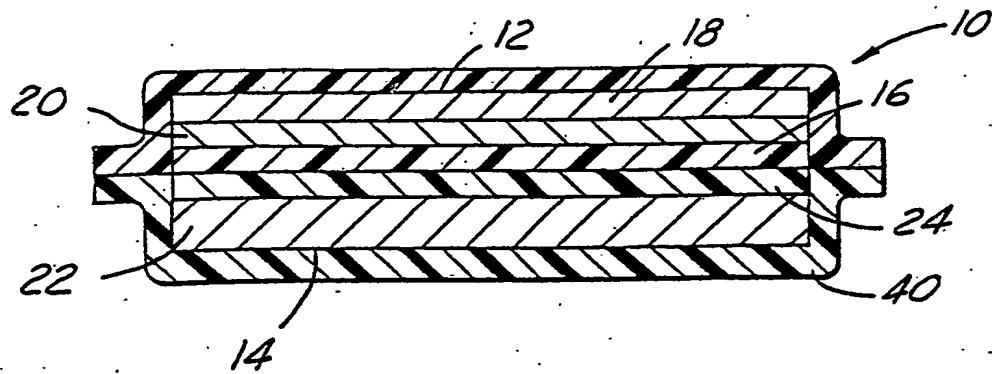


Figure 22

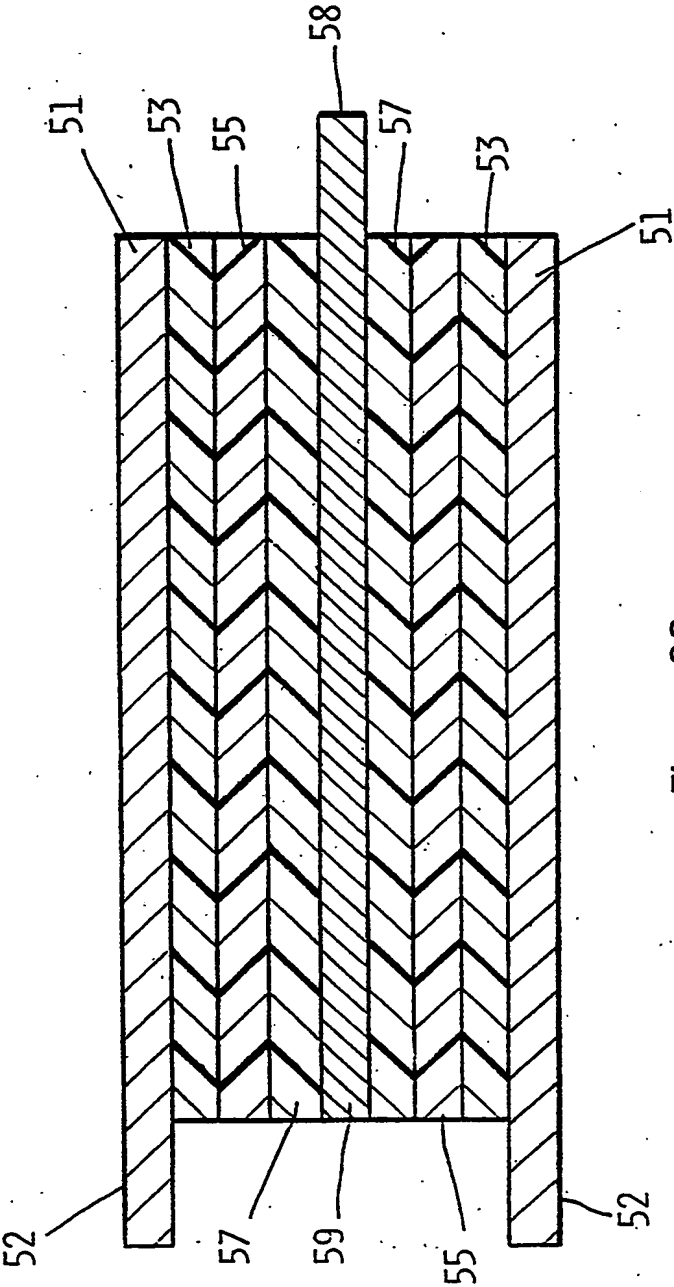


Figure 23

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C01B25/37 C01B25/45 H01M4/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C01B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

CHEM ABS Data, PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 12761 A (SAIDI MOHAMED YAZID ;BARKER JEREMY (US); VALENCE TECHNOLOGY INC (U) 26 March 1998 (1998-03-26) cited in the application the whole document	1-30
A	WO 00 01024 A (BARKER JEREMY ;VALENCE TECHNOLOGY INC (US)) 6 January 2000 (2000-01-06) the whole document	1-30
A	US 5 910 382 A (MASQUELIER CHRISTIAN ET AL) 8 June 1999 (1999-06-08) claims 1-9; examples 1,2	1-30

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

18 May 2001

Date of mailing of the international search report

28/05/2001

Name and mailing address of the ISA

European Patent Office; P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Siebel, E

Printed: 17-03-2004

INTERNATIONAL Cited Doc: WO 0153193A1 I

International Application Cited in: 01120637

Information on patent family members

PCT/US 00/35438

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9812761 A	26-03-1998	US 5871866 A	16-02-1999
		AU 4410297 A	14-04-1998
		EP 1093174 A	18-04-2001
		EP 0931361 A	28-07-1999
		JP 2001500665 T	16-01-2001
WO 0001024 A	06-01-2000	US 6136472 A	24-10-2000
		AU 4091899 A	17-01-2000
		EP 1090435 A	11-04-2001
US 5910382 A	08-06-1999	EP 0904607 A	31-03-1999
		JP 2000509193 T	18-07-2000
		WO 9740541 A	30-10-1997